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The structural behaviour of the nepheline family: (3) Thermal expansion of kalsilite

THE published structures of SrAl_2O_4 and BaAl_2O_4 (Schulze and Müller-Buschbaum, 1981; Hörkner and Müller-Buschbaum, 1979) and the change in the cell parameters of their solid solution series as a function of temperature and composition (Henderson and Taylor, 1982; Paper 1 of this series) indicated that their structural behaviour could be pictured in terms of two tilt systems. One (tilt 1) is a cooperative rotation of the framework tetrahedra about the three-fold axes which lie parallel to the c -axis, and the other (tilt 2) is a cooperative tilting of the framework tetrahedra relative to the 0001 plane. Both increasing temperature and increasing the size of the cavity cation were deduced to cause partial removal of both tilt systems. Distance Least Squares (DLS) modelling of the monoclinic $(\text{Ba,Sr})\text{Al}_2\text{O}_4$ solid-solution series has confirmed significant changes in both tilt systems for compositional effects, but smaller changes for thermal effects (Taylor *et al.*, 1985; Paper 2 of this series). It was not possible to explore the behaviour of the two tilt systems for the hexagonal $(\text{Ba,Sr})\text{Al}_2\text{O}_4$ solid-solution series by the DLS method because of severe problems in modelling their structures. For compositions close to, and including, BaAl_2O_4 the decreasing rate of thermal expansion of the c -axis indicated that removal of the second tilt system was reaching a limit (Henderson and Taylor, 1982). Unfortunately, it was not possible to explore this effect by further increasing the size of the cavity cation because Ba is the largest of the divalent, alkaline earth cations. However, the structures of the subcells of BaAl_2O_4 (Do Dinh and Bertaut, 1965; Uchikawa and Tsukiyama, 1966; Perrotta and

Smith, 1968) and kalsilite, KAlSiO_4 (Perrotta and Smith, 1965), show that they are in a similar state of structural collapse. Moreover, there is scope for increasing the cavity cation size in kalsilite by replacing some K by Rb. If sufficient replacement

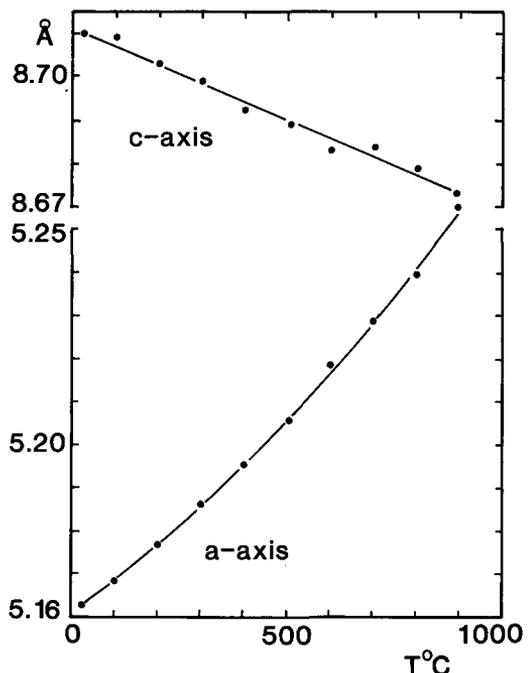


FIG. 1. Thermal expansion curves and observed data for synthetic kalsilite, KAlSiO_4 .

can take place then we would expect to see a decreasing rate of change of the *c*-axis as a function of increasing cavity cation size, perhaps even reaching a constant value. The thermal expansion behaviour of such compositions is expected to show little, if any, change in the *c*-axis and may even show a contraction of the *c*-axis.

The only reported infrared spectrum of kalsilite appears to be by Sahama (1965), and only covers the range 410 to 770 cm^{-1} for a natural specimen. The spectrum of the synthetic kalsilite used in this study was recorded in order to provide more complete data for the mineral and for comparison with the data reported by Sahama (1965).

TABLE 1. Thermal expansion data for kalsilite.

T, °C	a, Å	c, Å	V, Å ³
20 ⁺	5.1627(4)	8.7087(8)	201.02(3)
20	5.1624(5)	8.711(2)	201.04(4)
20 after 600	5.1642(5)	8.710(2)	201.17(4)
20*	5.1631(5)	8.710(2)	201.08(4)
20 after 890	5.1645(6)	8.704(2)	201.04(4)
100	5.1684(4)	8.709(1)	201.48(3)
200	5.1769(6)	8.703(2)	201.99(4)
300	5.1866(4)	8.699(1)	202.65(3)
400	5.1956(6)	8.692(2)	203.21(4)
505	5.2057(5)	8.689(1)	203.93(3)
600	5.2186(9)	8.683(2)	204.79(6)
700	5.2283(4)	8.684(1)	205.59(3)
800	5.2388(3)	8.679(1)	206.28(3)
890	5.2548(8)	8.673(2)	207.39(6)

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

Experimental methods. The specimen of kalsilite was synthesised from a gel starting material of composition KAlSiO_4 at 605 °C, 1 kb $P(\text{H}_2\text{O})$ for 5 days; kalsilite was the only phase detected in the run products by X-ray methods. Cell parameters at room temperature before the thermal expansion measurements were determined from X-ray dif-

fractometer charts (Cu-K α radiation) by the method of least squares with gallium arsenide as internal standard ($a = 5.654 \text{ \AA}$) using 17 kalsilite reflections. Indexing was based on the data of Perrotta (1965). The cell parameters at elevated temperatures and at room temperature after heating were determined by using between 12 and 15 kalsilite reflections and with reflections from the Pt sample holder as internal standard (Henderson and Taylor, 1975).

The infrared spectrum was recorded on a Perkin Elmer 577 double-beam grating spectrometer by the alkali halide disc method (1.3 mg of specimen to 200 mg of KBr) over the range 200 to 4000 cm^{-1} . For sharp absorption bands the reported wavenumbers are within $\pm 2 \text{ cm}^{-1}$ and for broad absorption bands within $\pm 5 \text{ cm}^{-1}$.

Results. The *a*- and *c*-parameters at room temperature are slightly larger than those obtained by Ferry and Blencoe (1978). Thermal expansion data for kalsilite are given in Table 1 and regression data in Table 2. The fitted thermal expansion curves are shown in Fig. 1 with the observed data. The results show a moderate expansion of the *a*-axis and the volume and a contraction of the *c*-axis on heating. The kalsilite peaks at 890 °C show a reduction in intensities of 20–30% relative to their intensities at 20 °C before the heating experiments and to their intensities at 800 °C. Some peaks also show a distinct broadening, but no new peaks were observed. The intensities and peak widths at 20 °C after 890 °C are identical to those before the experiments.

The infrared spectrum is shown in Fig. 2, and the absorption bands at 460 and 688 cm^{-1} are in good agreement with the limited data given by Sahama (1965) for a natural specimen. No absorption bands were observed between 1300 and 4000 cm^{-1} .

Discussion and conclusions. The thermal behaviours of the *a*- and *c*-axes are significantly different from their compositional behaviour (Fig. 3). The compositional data of Ferry and Blencoe (1978) show that the *a*- and *c*-axes increase as Na is

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

	Y_0	$10^6 x_1$	$10^9 x_2$	R	SE
a, Å	5.1615	13.6(11)	7.1(12)	0.9992	0.0014
c, Å	8.7113	-4.87(24)		0.9907	0.0018
V, Å ³	201.01	21.6(18)	15.2(19)	0.9994	0.084

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.

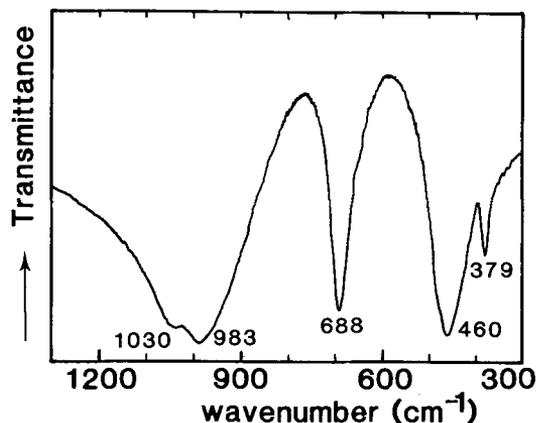


FIG. 2. Infrared spectrum of synthetic kalsilite giving the wavenumbers of the absorption bands.

replaced by K in the $(\text{Na,K})\text{AlSiO}_4$ kalsilite solid-solution series. In contrast, in end-member kalsilite, heating gives rise to a greater rate of change of the a -axis as a function of the molar volume and the c -axis contracts. Both of these thermal trends clearly diverge from the compositional trends (Fig. 3). The contraction of the c -axis of kalsilite is unusual, but not unexpected. By analogy with the hexagonal $(\text{Ba,Sr})\text{Al}_2\text{O}_4$ solid solution series (Henderson and Taylor, 1982) it appears that removal of the second tilt system (tilt 2) has reached a limit in kalsilite and that the structure along the c -axis of kalsilite is in a fully-expanded state at room temperature. This further suggests that solid solution of kalsilite with RbAlSiO_4 is likely to be limited in extent. End-member kalsilite is, therefore, in a more expanded structural state than BaAl_2O_4 . It will be interesting to study the effect of the substitution of Na for K on thermal expansion behaviour.

It seems likely that the peak changes observed at 890°C represent the onset of a reversible inversion to a high-temperature kalsilite polymorph. Andou and Kawahara (1982) placed the inversion temperature at 865°C and our results are consistent with this estimate.

Sahama (1965) noted that the infrared absorption band lying between 500 and 520 cm^{-1} in the nephelines could be used as an indicator of the potassium content. Extrapolation of Sahama's equation for perpotassic nephelines would place this absorption band at 484 cm^{-1} in pure kalsilite. Although, there is an ill-defined shoulder on the 460 cm^{-1} band between 475 and 490 cm^{-1} , the spectrum of kalsilite is simpler than that of nepheline and this diagnostic band may be absent

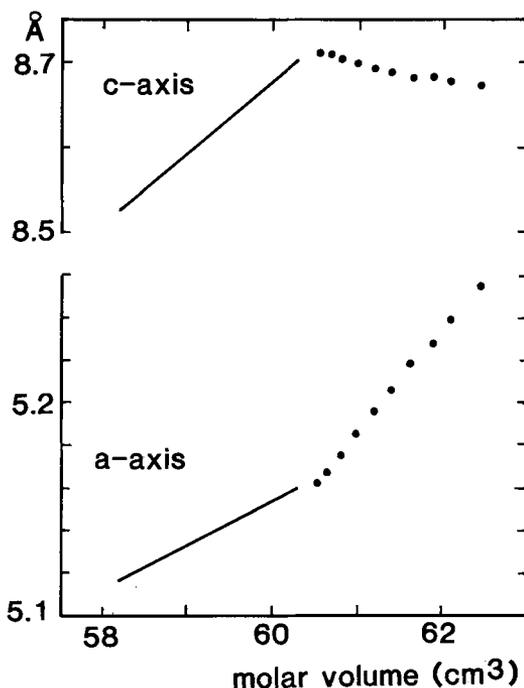


FIG. 3. The compositional trends of the a - and c -axes of the $(\text{Na,K})\text{AlSiO}_4$ kalsilite solid solutions (solid lines; data of Ferry and Blencoe, 1978) compared with the thermal trends of synthetic kalsilite (full circles; this work).

or merged with the relatively broad band at 460 cm^{-1} . The wavenumber of the 983 cm^{-1} absorption band is consistent with the relationship noted between the main absorption band of framework structures and the average T -O distance and T -O- T angle (Henderson and Taylor, 1979; T represents the tetrahedrally-coordinated cations in the framework).

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Reyerite, tobermorite, calcian analcime and bytownite from amygdalites in a Skye basalt

A ROAD realignment scheme at the bridge over the Allt Coir' a' Ghobhainn (NG 407322) on the A863, near Drynoch, has cut into two distinctive lava types on the northern side of the road. To the west of the bridge greyish-green, highly amygdaloidal basaltic lavas contain abundant analcime whereas dark, compact lavas with relatively few amygdalites form a 30 foot high cliff to the east. Derived from the latter are loose blocks which contain amygdalites infilled predominantly by a pearly, gyrolite-like mineral together with tobermorite and a greyish, extremely hard, porcelainous phase. The latter, which frequently lines larger amygdalites or fills smaller amygdalites, is an intergrowth of calcian analcime and bytownite. X-ray powder diffraction and infrared methods identify the gyrolite-like phase as the rare species reyerite cf. closely related truscottite.

A number of hydrated calcium silicates—gyrolite, okenite, reyerite, tacharanite, tobermorite, and xonotlite—have been previously reported by Walker (1971) in olivine basalts of Mull and Morven. Sweet (1961) discovered tacharanite, gyrolite and tobermorite in an olivine dolerite outcropping just north of Portree, Skye, and Cann (1965) noted reyerite filling slightly metamorphosed amygdalites at 'S Airde Beinn, 5 km west of Tobermory, Mull.

Olivine basalt

Thin section examination of this dark, compact rock reveals a groundmass with microporphyrictic

olivine and pyroxene, the former exhibiting varying degrees of serpentinization. An electron probe analysis of groundmass olivine yielded the following composition: SiO_2 37.8, Al_2O_3 0.1, FeO 23.9, MnO 0.4, CaO 0.4, and MgO 37.7 wt. % indicating Fo 73.7 mol. %. A groundmass plagioclase analysis reduces to $\text{Or}_{1.1}\text{Ab}_{30.7}\text{An}_{68.2}$. From these compositions it is deduced that in a dry system, at one atmosphere, liquidus plagioclase forms at 1220 °C and olivine at 1150 °C (Russell, pers. comm.). An X-ray fluorescence analysis (EDS) of the basalt gave the following results: SiO_2 48.45, TiO_2 1.61, Al_2O_3 16.31, FeO 10.68 (total Fe as FeO), MnO 0.14, MgO 7.71, CaO 10.47, Na_2O 1.73, K_2O 0.37 and loss on ignition 2.86 wt. % [total 100.33].

Reyerite and tobermorite

Reyerite is micaceous and infills central zones within the amygdalites. Tobermorite occurs as the 11 Å phase. It forms highly fibrous, radiating sheaves or rosettes, the latter up to 0.4 cm radius. Minor associated minerals in these reyerite-bearing amygdalites are chlorite, calcite, pectolite and thomsonite.

Electron probe analyses of reyerite and tobermorite are presented in Table 1. It is noteworthy that when reyerite analyses are normalized to 24 (Si + Al) atoms per formula unit close to 10% of the tetrahedral sites are filled with Al. The same degree of site occupancy was reported by Clement and Ribbe (1973) in Virginian reyerite and, additionally, by Cann (1965). Analyses 1 and 4