The thermal expansion of the sodalite group of minerals

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Summary. Thermal expansion data up to 920° C by powder X-ray diffraction methods are presented for four noseans, five haüynes, and one sodalite. The rate of thermal expansion is at first high and increases with temperature; this is interpreted as due to the untwisting of the partially collapsed framework. Above a certain temperature (which depends on the mineral and its composition) the rate of thermal expansion is much lower and is linear with temperature; this corresponds to the rate of thermal expansion of the more fully expanded framework. Sodalite does not show this second stage below 920° C. The thermal expansion behaviour of other framework silicates is interpreted in analogy to that of the sodalite group.

The thermal expansion behaviour of the framework silicates poses interesting problems. Consisting essentially of a partially covalently bonded three-dimensional framework, they might be expected to have low thermal expansion rates. Unfortunately, there has been little detailed work on the thermal expansion of framework silicates, apart from the silica minerals and the feldspars. The simple picture of a three-dimensional framework is complicated by the fact that their frameworks show varying degrees of collapse at room temperature, which depend on the interframework ions (except for silica). A detailed study of the thermal expansion of the sodalite group of minerals might be expected to give a general understanding of the thermal expansion of framework silicates.

The members of the sodalite group of minerals have essentially the same aluminosilicate framework ($Al_6Si_6O_{24}$). Dependent on whether chlorine or sulphate is the predominant interframework anion, the common rock-forming sodalite minerals can be divided into sodalite proper ($Na_8Al_6Si_6O_{24}Cl_2$) and the nosean–haüyne solid solution series $(Na_{5-8}K_{0-1}Ca_{0-2}\square_{0-1})_8(Al_6Si_6O_{24})(SO_4)_{1-2}\,.\,nH_2O$. According to Taylor (1967) haüyne possesses the space group $P\bar{4}3n$ and is richer in calcium and sulphate than nosean, which possesses the space group $P\bar{4}3m$. The specimens used in this study are taken from the series of sodalite

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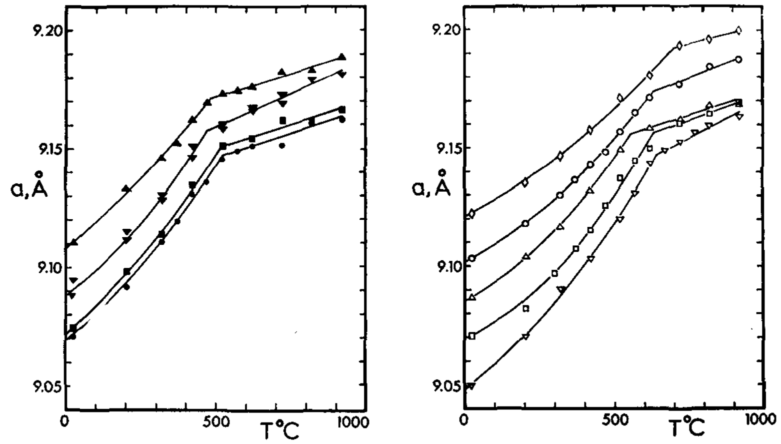
minerals described elsewhere (Taylor, 1967), and the same numbers have been retained. Specimen no. 5, which initially was sharply zoned, was homogenized by heating at 1000° C for one day.

Experimental procedure. The diffraction furnace used was one 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 inversion points 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 silicate specimens were determined from peaks in the range 50° to 77° 2θ (Cu-$K\alpha_1$) at various temperatures between 25° and 920° C and refined by least squares.

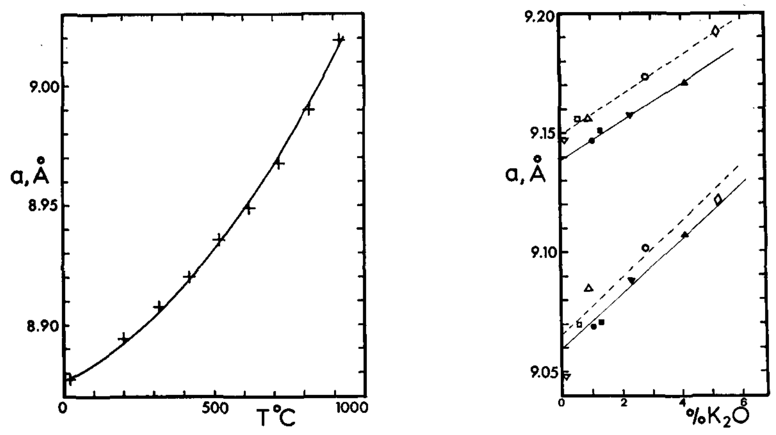
Results. The values of the cell parameter a as a function of temperature are given in table I and plotted in fig. 1 (*a*), (*b*), and (*c*); the cell parameters are believed to be accurate to $\pm 0{\cdot}003$ Å and the temperature $\pm 3°$ C. That the X-ray effects are reversible is shown by specimen no. 2 for which cell parameters were first obtained at successively lower temperatures from 720° to 25° C, and secondly at successively higher temperatures from 25° to 920° C. It is believed that no chemical changes take place as a result of the heating, apart from the loss of 'zeolitic' water, since after dehydration experiments at 1250° C (Taylor, 1967) there was no evidence of loss of either sulphate or chlorine, the weight loss being accounted for wholly by water. However, slight changes in the cell parameters were reported, comparable with those recorded here for the 25° C runs before and after the heating experiments. These changes might be due to the water loss, but do not significantly affect the present results and their interpretation.

It is evident from figs. 1 (*a*) and 1 (*b*) that there is a large change in the thermal expansion rate for the noseans and haüynes in the temperature range studied. It is not certain that the change in the expansion rate is sharply defined, but this has been assumed, and the supposed temperature at which the discontinuity takes place will be referred to as T_d. For temperatures below T_d the data were fitted by the method of least squares to the polynomial equation: $a = a_o\,(1+bT+cT^2)$, where a is the cell edge at a temperature $T°$ C and a_o the cell edge at 0° C. The discontinuity temperature T_d and the cell edge a_d at that temperature were determined by finding the intersection of the fitted curve with a straight line fitted to the points above that temperature. The un-



(a) NOSEANS

(b) HAÜYNES



(c) SODALITE

(d)

FIG. 1. Thermal expansion curves for: a, noseans; b, haüynes; and c, sodalite. Noseans, 2 ▼, 5 ▲, 6 ■, 21 ●; haüynes, 1 □, 4 △, 16 ▽, 22 ◇, 23 ○; sodalite, 19 +. d: relationship between the K_2O content and the cell edge at 25° C and at the temperature T_d for noseans and haüynes.

certainty involved is believed to be ±0·003 Å for the cell edge and ±5° C for the temperature. The calculated constants are given in Table II.

Four apparently significant observations can be deduced from the thermal expansion data for the nosean–haüyne minerals. There is

TABLE I. Cell edges of sodalite minerals at selected temperatures (all data in Å)

T	Noseans					Haüynes					Sodalite
	2(*c*)*	2(*h*)*	5†	6	21	1	4	16	22	23	19
25° C	9·094	—	9·110	9·074	9·070	9·071	9·087	9·049	9·122	9·103	8·877
25§	9·088	9·088	9·110	9·082	9·074	9·074	9·086	9·050	9·123	9·105	8·866
205	9·115	9·111	9·133	9·098	9·092	9·082	9·104	9·070	9·135	9·118	8·894
320	9·130	9·128	9·146	9·114	9·110	9·097‡	9·117	9·090	9·146	9·130	8·907
370	—	—	9·152	—	9·119	9·107	—	—	—	9·137	—
420	9·151	9·146	9·162	9·135	9·131	9·115	9·131	9·103	9·157	9·143	8·920
470	—	—	9·169	—	9·136	9·126	—	—	—	9·148	—
520	9·158	9·160	9·173	9·151	9·145	9·137	9·149	9·120	9·171	9·157	8·936
570	—	—	9·175	—	9·149	9·144	—	9·131	—	9·165	—
620	9·167	9·166	9·176	9·154	9·151	9·150	9·158	9·144	9·180	9·171	8·949
670	—	—	—	—	—	—	—	9·149	—	—	—
720	9·168	9·173	9·182	9·162	9·151	9·160	9·162	9·153	9·194	9·177	8·968
770	—	—	—	—	—	—	—	9·157	—	—	—
820	—	9·179	9·183	9·162	9·160	9·164	9·168	9·159	9·196	9·184	8·990
920	—	9·181	9·188	9·167	9·162	9·169	9·168	9·163	9·200	9·187	9·019

* *c* and *h* refer to data obtained at successively lower and higher temperatures respectively.

† Nosean homogenized prior to experiment by heating at 1000° C *for* 1 *day.*

§ Cell edge obtained at 25° C after experiment.

‡ Cell edge at 300° C.

TABLE II. Thermal expansion data for the sodalite minerals. α_l is the mean linear expansion coefficient over the range 0 to T_d° C, and α_h above T_d

	a_0	$b \times 10^6$	$c \times 10^9$	$\alpha_l \times 10^5$	$\alpha_h \times 10^5$	T_d	a_d
Noseans							
2*	9·089 Å	9·21	14·78	1·61	0·65	465° C	9·157 Å
5	9·108	11·43	6·25	1·45	0·40	485	9·172
6	9·072	12·16	9·22	1·69	0·43	515	9·151
21	9·069	11·37	9·95	1·66	0·42	525	9·148
Haüynes							
1	9·070	5·56	15·11	1·51	0·49	630	9·156
4	9·086	7·03	12·24	1·39	0·45	555	9·156
16	9·048	10·35	10·23	1·70	0·76	645	9·147
22	9·121	7·08	5·97	1·11	0·35	700	9·192
23	9·102	6·93	8·86	1·26	0·56	630	9·174
Sodalite							
19	8·876	6·69	11·28	—	—	—	—

* These values were obtained from the heating and cooling data for this specimen in table I.

a change at a temperature T_d, in the range 460 to 530° C for the noseans and 550° to 700° C for the haüynes studied, from a relatively high, increasing rate of expansion to a low, constant rate of expansion (table II and fig. 1). Below the temperature T_d the haüynes have a lower mean expansion coefficient than the noseans with similar K_2O contents (fig. 2). Below the temperature T_d the potassium-rich minerals have a lower mean expansion coefficient than the potassium-poor minerals with similar CaO contents (fig. 2). The cell edge a_d at the temperature T_d appears to be related to the CaO and K_2O contents (fig. 1 (*d*) and

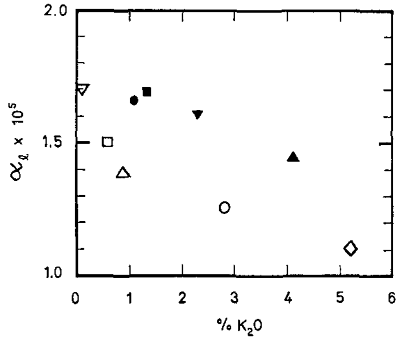


FIG. 2. The relationship between the mean thermal expansion coefficient for the temperature range 0° to T_d° C, and the K_2O content for noseans and haüynes. Symbols as in fig. 1.

below), since the haüynes (calcium-rich) plot above the noseans (calcium-rich) with similar K_2O contents, and the cell edge increases for both noseans and haüynes with increase in the K_2O content.

Interpretation of the results. The effect of heating on the structure of α-quartz, which is partially collapsed due to the rotation of the silica tetrahedra, will first be considered. The high rate of thermal expansion observed for α-quartz, compared with β-quartz, 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 there is no apparent change greater than 0·001 Å in the Si–O bond length. One might assume then that the thermal expansion observed in α-quartz up to the inversion temperature is due principally to the rotation of the tetrahedra from the collapsed state, the expansion of the Si–O bond making a negligible or very small contribution.

Thus the first interpretation of the expansion curves for the sodalite group of minerals was that the cell edge increased by rotation of the framework tetrahedra until the framework attained an expanded state; thereafter the expansion was determined by that of the framework bonds, and was thus relatively small. If the framework of the nosean–haüyne minerals were fully expanded above the temperature T_d, the cell edge would be approximately 9·31 Å, and the structure of haüyne would become body-centred ($I\bar{4}3m$). The 210 reflection of haüyne is the most intense reflection on the powder diffraction pattern for which $h+k+l \neq 2n$; the intensity of this reflection relative to that of the 211 reflection was determined for several haüynes throughout the temperature range studied. Although in some cases the relative intensity of the 210 reflection decreased, the peak did not disappear in any of the specimens studied. The lack of a change of space-group for haüyne, and the fact that the observed values of the cell edge of the nosean–haüyne minerals at the discontinuity temperature T_d ranged from 9·14 to 9·20 Å (extrapolation of the high-temperature line to room temperature would bring a to about 9·10 to 9·17 Å), shows that the ideal full expansion cannot have been attained.

The significant variation in the cell edge a_d at the temperature T_d is difficult to explain in detail. It was at first supposed to be due to the small variation in the Si:Al ratios of the minerals, but as the fully expanded state is not attained, small variations in the Si:Al ratio are unlikely to affect a_d significantly. An explanation must be sought in the presence of the other cations and anions in the structure, which prohibit its full expansion to the theoretical uncollapsed state. In fact the variation in the value of a_d can be related to the CaO and K_2O contents of the minerals by the equation:

$$a_d = 9{\cdot}138+1{\cdot}586\times 10^{-3}(\%\text{CaO})+7{\cdot}293\times 10^{-3}\,(\%\text{K}_2\text{O})\pm 0{\cdot}002\ \text{Å},$$

where 9·138 Å is the value of a_d for pure nosean. The interpretation of this is that the framework (and hence the Si:Al ratio) gives the unit cell its gross size, but the actual size is determined by the proportion and nature of the interframework ions. The difference in space-group between nosean ($P\bar{4}3m$) and sodalite and haüyne ($P\bar{4}3n$) must also depend on the nature, number, and position of these interframework ions, as the framework in these minerals has almost the same composition. As the large holes in the structures of sodalite and haüyne are more fully occupied by large anions (Cl and SO_4) than in nosean, the cations in the former are presumably more tightly bound to the framework (the lower expansion coefficients for sodalite and haüyne than for nosean may confirm this). Again, the much larger size of the potassium ion may expand the cell at lower temperatures, accounting for the lower expansion coefficients for potassium-rich minerals and for the higher values of a_d (table II).

The interpretation of the thermal expansion curves is, therefore, that the expansion is principally due to the rotation of the framework tetrahedra, but the degree of expansion by this method is restricted at a temperature T_d by the bonds of the framework oxygens with the interframework cations. The substitution of K for Na allows the framework to expand further from the collapsed state because of the much larger ionic radius of potassium and because of its weaker bonds. This interpretation accounts for the strong dependence of a_d on the contents of CaO and K_2O. The value of a_d expected for specimen no. 19 (sodalite) should be of the same order as, or less than that of potassium-poor noseans and haüynes, which presumably explains why no discontinuity is observed in its expansion curve up to 920° C.

Comparison with other framework silicates. In concluding, the interpretation applied to the thermal expansion curves of the sodalite minerals will be examined with reference to other framework silicates. It is anticipated that the majority of framework silicates will show some degree of collapse, or distortion, of their frameworks, since it is unlikely that the interframework ions will have exactly the ionic radii to hold the framework in an expanded state. It is already known that some minerals, e.g. leucite (Wyart, 1937) and sodium-rich alkali feldspars

(MacKenzie, 1952), show structural inversions on heating. Such inversions do not necessarily mean that an ideal uncollapsed state has been achieved. As expansion data are available for some of the framework silicates, it is interesting to examine them in the light of the present interpretation.

Cristobalite. The following discussion is based on the data given by Johnson and Andrews (1956). Tetragonal α-cristobalite shows an almost linear thermal expansion and inverts to the cubic β-form at 218° C, accompanied by a discontinuity in the expansion. The rate of linear expansion of β-cristobalite in the interval 218° to 400° C increases from $0{\cdot}90\times10^{-5}$ for the range 219° to 270° C to $1{\cdot}18\times10^{-5}$ for the range 270° to 330° C, and the mean for the range 219° to 330° C is relatively high ($1{\cdot}05\times10^{-5}$). This presumably indicates that the cubic polymorph is still in a state of partial collapse after the inversion. It only reaches an uncollapsed state at approximately 400° C, since after 400° C the expansion rate is low ($0{\cdot}14\times10^{-5}$) and constant up to the maximum temperature recorded (1138° C). This low expansion rate is presumably due to the expansion of the partly covalent Si–O bonds. This interpretation indicates that the structure of β-cristobalite is partially collapsed at 219° C, which is in agreement with the structural determinations (Deer, Howie, and Zussman, vol. 4, 1963); β-cristobalite should achieve the idealized cubic structure (Wyckoff, 1925) at 400° C. It is assumed that in the silica minerals the absence of interframework ions allows the framework to achieve the ideal fully expanded state.

Nepheline. According to Sahama (1962), who studied the thermal expansion of two nephelines, the expansion is approximately linear in the temperature range 25° to 900° C, and the average of the mean linear expansion coefficient for this range is $1{\cdot}69\times10^{-5}$. This high coefficient, taken with the evidence that the structure is distorted at room temperature, suggests that the expansion is due to the partial removal of the distortions in the structure. It is possible that at higher temperatures there may be a change in the rate of expansion to a lower value consistent with the attainment of an undistorted structure.

Leucite shows a structural transformation from a tetragonal to a cubic form at temperatures around 650° C (Wyart, 1937; Faust, 1963). From investigations now in progress it appears that natural leucite achieves an uncollapsed state (i.e. the maximum expansion by rotation of the framework tetrahedra permitted by the interframework cations) at the inversion, since the mean linear expansion coefficient above the inversion temperature is relatively low ($0{\cdot}3\times10^{-5}$).

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