MINERALOGICAL MAGAZINE, SEPTEMBER 1979, VOL. 43, PP. 429-31

The thermal expansion of aluminate- and aluminogermanate-sodalites

C. M. B. HENDERSON AND D. TAYLOR[1]

Department of Geology, The University, Manchester M13 9PL

SYNOPSIS

DISCONTINUITIES occurring in the expansion behaviour of aluminosilicate-sodalites with large cavity anions such as I^- and SO_4^{2-} are thought to occur when the coordinate of the cavity cation becomes 0.25 (Henderson and Taylor, 1978). We also suggested that further thermal expansion work could explore how the disposition of sodalites in a diagram such as fig. 4 of Henderson and Taylor relates to the presence or absence of discontinuities.

We have now studied the expansion of three more sodalites which were expected to show discontinuities, namely one aluminogermanate-sodalite ($Na_8(Al_6Ge_6O_{24})I_2$) and two aluminate-sodalites ($(Sr_8(Al_{12}O_{24})(CrO_4)_2$ and $Sr_2Ba_6(Al_{12}O_{24})(SO_4)_2$). $Sr_8(Al_{12}O_{24})(CrO_4)_2$ was thought to have an ~ 9 Å cubic cell at room temperature but the occurrence of broadened and split reflections in our sample suggests that this is not the case. Stepwise heating experiments on our sample showed the presence of a reversible, presumably displacive, transformation at 40 ± 2 °C above which the X-ray reflections were sharp.

All three sodalites showed significantly smaller expansion rates than for aluminosilicate-sodalites having similar degrees of structural collapse. The lower mean expansion coefficient (0-500 °C) for $Na_8(Al_6Ge_6O_{24})I_2$ of $12.5 \times 10^{-6}C^{-1}$ compared with that for $Na_8(Al_6Si_6O_{24})I_2$ of $15.1 \times 10^{-6}C^{-1}$ is particularly significant as the only chemical difference between these two phases is substitution of Ge for Si. In addition none of the three sodalites showed the discontinuities expected and this suggests that the low expansion rates do not allow the cavity cation to reach a coordinate of 0.25 over the temperature range investigated.

Our earlier concept of the mechanism of expansion of the sodalite structure assumed that the expansion of the cavity cation-cavity anion bond forced the cavity cations against and between the framework oxygens so untwisting the partially collapsed structure (Henderson and Taylor, 1978). It now appears that this concept was oversimplified and that the expansion characteristics of sodalites depend on the nature of the tetrahedrally coordinated framework cations present as well as on the cavity cations and anions.

REFERENCE

Henderson (C. M. B.) and Taylor (D.), 1978. *Phys. Chem. Min.* **2**, 337-47.

[*Manuscript received 14 December 1978*]

---

[1] Present address: 15 Leigh Road, Congleton, Cheshire.

THE THERMAL EXPANSION OF ALUMINATE- AND ALUMINOGERMANATE-SODALITES

C.M.B. Henderson and D. Taylor

Department of Geology, The University, Manchester M13 9PL.

The thermal expansion behaviour of the aluminosilicate-sodalites has been interpreted by means of a computer model of the cubic sodalite structure (Henderson and Taylor, 1978). It was concluded that a discontinuity should only be expected for aluminosilicate-sodalites containing large cavity anions, for example I^- and SO_4^{2-}, and that the discontinuity occurs when the coordinate of the cavity cation becomes 0.25. It was suggested that further thermal expansion work might explore how the disposition of sodalites in a diagram such as figure 4 of Henderson and Taylor (1978) relates to the presence or absence of discontinuities.

This paper is one such study and examines the expansion behaviour of two aluminate-sodalites and one aluminogermanate-sodalite.

Experimental procedure. The specimen of $Sr_8(Al_{12}O_{24})(CrO_4)_2$ was provided by Professor F.A. Hummel of Pennsylvania State University and the specimen of $Na_8(Al_6Ge_6O_{24})I_2$ by Dr. D.J. Schipper of Philips, Eindhoven. The specimen of $Sr_2Ba_6(Al_{12}O_{24})(SO_4)_2$ was synthesised from an appropriate mixture of commercial gibbsite and barium carbonate and general-purpose laboratory-grade strontium sulphate by heating twice at 1400°C for 4 h. The experimental procedure for determining the expansion curves is given by Henderson and Taylor (1975) and the analysis of the data follows the procedures used by Henderson and Taylor (1978).

Results. The compositions of the sodalites and their cell parameters at room temperature and elevated temperatures are given in Table I. Thermal expansion curves are shown in figure 1.

Table I. Cell parameters of synthetic sodalite minerals at room temperature and elevated temperatures

The arrangement of the entries in the Table is : temperature (°C), cell edge Å (estimated standard deviation x 10^4 Å)

(1) $Na_8(Al_6Ge_6O_{24})I_2$: 20, 9.1827(11); 20 after 700, 9.1834(7); 20 after 1015, 9.1842(8); 150, 9.1948(13); 305, 9.2133(8); 410, 9.2286(6); 510, 9.2437(14); 615, 9.2616(17); 710, 9.2764(25); 755, 9.2861(17); 805, 9.2944(15); 860, 9.3048(6); 910, 9.3175(11); 950, 9.3312(17); 1015, 9.3524(20).

(2) $Sr_8(Al_{12}O_{24})(CrO_4)_2$: 20, 9.4409(15); 20 after 1020, 9.4371(15); 150, 9.4510(11); 300, 9.4621(16); 400, 9.4669(14); 495, 9.4728(13); 600, 9.4806(17); 705, 9.4849(8); 805, 9.4906(17); 910, 9.4989(17); 1020, 9.5066(16).

(3) $Sr_2Ba_6(Al_{12}O_{24})(SO_4)_2$: 20, 9.5465(27); 20 after 905, 9.5436(10); 150, 9.5542(24); 295, 9.5584(19); 400, 9.5657(21); 505, 9.5732(26); 610, 9.5773(20); 705, 9.5878(20); 805, 9.5920(26); 905, 9.5982(21).

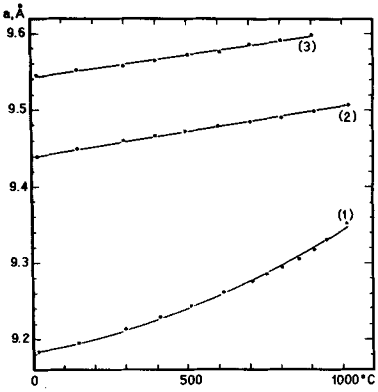

Fig. 1. Thermal expansion relationships for :
(1) $Na_8(Al_6Ge_6O_{24})I_2$, (2) $Sr_8(Al_{12}O_{24})(CrO_4)_2$ and (3) $Sr_2Ba_6(Al_{12}O_{24})(SO_4)_2$.

Table II. Regression data for thermal expansion curves

Specimen Number	a_0, Å	10^6b	10^6S_b	10^9_c	10^9S_c	R	SE, Å	$10^6\alpha$, C^{-1}
1	9.1825	7.63	± 0.89	9.80	± 0.87	0.9990	0.0028	12.5
2	9.4385	7.85	± 0.61	-0.95	± 0.64	0.9976	0.0018	7.4
2*	9.4397	6.95	± 0.18			0.9969	0.0019	6.9
3	9.5444	5.24	± 0.72	1.15	± 0.84	0.9966	0.0018	5.8
3*	9.5432	6.29	± 0.21			0.9955	0.0019	6.3

S_b and S_c are the standard errors of the regression coefficients b and c; R is the multiple correlation coefficient; SE the standard error of the estimate; and α the mean linear expansion coefficient between 0° and 500°C.
* linear fits.

The thermal expansion curves were fitted by least squares to a second order polynomial and subsequently modified to the form: $\underline{a} = \underline{a}_0\,(1 + bT + cT^2)$. The values of $\underline{a}_0$, b and c are given in Table II with mean expansion coefficients, $\Delta\underline{a}/(\underline{a}_0\Delta T)$, for the range 0 to 500°C. Student's t-tests showed that the c-regression coefficients for sodalites 2 and 3 were not significantly different from zero and so the expansion data for these specimens is more appropriately fitted by a straight line, $\underline{a} = \underline{a}_0\,(1 + bT)$. Accordingly, linear regression data are also given for these specimens in Table II.

Many aluminate-sodalites do not have a cubic ~9Å unit cell (Halstead and Moore, 1962; Saalfeld and Depmeier, 1972; Depmeier, 1977) which complicates the thermal expansion behaviour by giving rise to displacive transformations (Depmeier, 1977). The aluminate-sodalites used in this study were selected because they apparently had cubic ~9Å unit cells and, therefore, any discontinuities observed could not be caused by transformations to an ~9Å cubic structure. However, during the course of the work it became clear that specimen No. 2 was not truly cubic. The effect was noted at diffraction angles above 60° 2Θ Cu K_α and consisted of splitting of certain reflections giving rise to broadened peaks or apparent Cu $K\alpha_2$ components with too high relative intensities (figure 2). Three diffraction peaks were examined: 444 which showed no effect, 620 which showed broadening and 622 which developed an anomalous Cu $K\alpha_2$ component. At the first temperature on the expansion curve, 150°C, the broadening or splitting had disappeared and the 622 reflection was resolved into Cu $K\alpha_1$ and α_2 components with normal relative intensities (figure 2). The 444, 620 and 622 peaks were, therefore, scanned at decreasing and increasing temperatures to locate the temperature at which specimen No. 2 became truly cubic. The transformation temperature was found to be 40° ± 2°C, with practically no hysteresis. Although not explored in detail this transformation appears to have little, if any, effect on the expansion behaviour.

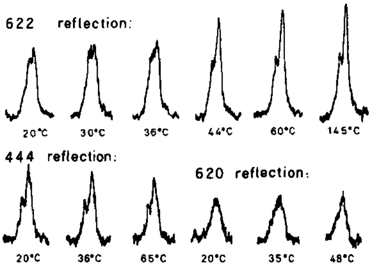

Fig. 2. Profiles of the 444, 620 and 622 X-ray diffraction peaks of $Sr_8(Al_{12}O_{24})$-$(CrO_4)_2$ at different temperatures. The profile of the 444 reflection does not change, that of the 620 reflections loses its broadening, and that of the 622 reflection shows resolution of the Cu $K\alpha_1$ and α_2 components.

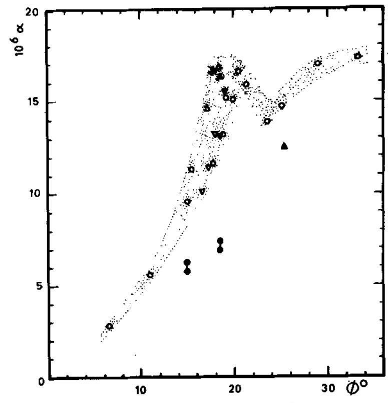

Fig. 3. Mean linear expansion coefficients (0 to 500°C), $\Delta\underline{a}/(\underline{a}\Delta T)$, for various sodalites as a function of the room-temperature tilt angle, ϕ, of the framework tetrahedra. The value of ϕ was obtained from figure 7 of Taylor and Henderson (1978). The data points for the aluminosilicate-sodalites (open symbols) fall in the shaded area. Symbols : o halide-bearing aluminosilicate-sodalites, △ noseans, ▽ haüynes, ● aluminate-sodalites, ▲ aluminogermanate-sodalites.

Discontinuities were not observed in the expansion curves over the temperature ranges studied (figure 1). The mean expansion coefficients for these sodalites (Table II) are lower than those of most aluminosilicate-sodalites (Henderson and Taylor, 1978). It is important to realise that the expansion coefficients of sodalites with different sized fully-expanded structures should be compared for similar degrees of structural collapse rather than for similar room-temperature cell edges. The need for this arises because of the dependence of the cell edge on the cosine of the tilt angle, ϕ, of the framework tetrahedra (Taylor, 1972). Depending on whether ϕ is large or small similar absolute changes in ϕ will have respectively large or small effects on $\underline{a}$ (Henderson and Taylor, 1978) and hence on the mean expansion coefficient. Thus, in figure 3, the mean expansion coefficients (0 to 500°C, Table II), including values calculated from the data of Taylor (1968) and Henderson and Taylor (1978), are shown plotted against ϕ, the values for which were estimated from figure 7 of Taylor and Henderson (1978). The mean expansion coefficients for the aluminogermanate- and aluminate-sodalites are significantly smaller than those for aluminosilicate-sodalites with similar ϕ values.

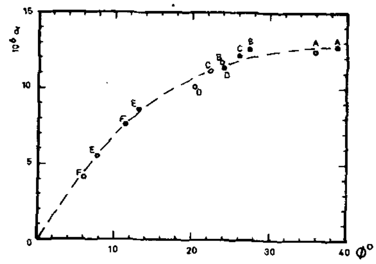

Fig. 4. Mean calculated expansion coefficients (0 to 500°C), α, for sodalites $\underline{M}_8(\underline{T}_{12}O_{24})\underline{X}_2$ as a function of the tilt-angle, ϕ. The calculations assumed an expansion in the $\underline{M}$-$\underline{X}$ bond of 2.54% between 0° and 500°C, and are more fully explained in Henderson and Taylor (1978). The open symbols represent sodalites with $(Al_6Si_6O_{24})^{6-}$ frameworks and the closed symbols $(Al_6Ge_6O_{24})^{6-}$ frameworks. (A) $\underline{M}$ = Li, $\underline{X}$ = Cl; (B) $\underline{M}$ = Na, $\underline{X}$ = Cl; (C) $\underline{M}$ = Na, $\underline{X}$ = Br; (D) $\underline{M}$ = Na, $\underline{X}$ = I; (E) $\underline{M}$ = K, $\underline{X}$ = Cl; (F) $\underline{M}$ = K, $\underline{X}$ = Br.

Discussion and conclusions. We expected the thermal expansion behaviour of the aluminate- and aluminogermanate-sodalites to be similar to that of the aluminosilicate sodalites and so constructed a diagram for Al-O and Al, Ge-O framework bonds (assuming both distances to be 1.747Å) analogous to that of figure 4 of Henderson and Taylor (1978). Lines of constant cation:anion radius ratio (Henderson and Taylor, 1978) were plotted on this diagram for three sodalites, $Na_8(Al_6Ge_6O_{24})\underline{X}_2$ with $\underline{X}$ = Cl, Br, or I. Those for the I- and Br-bearing sodalites intersect the boundary of the sodalite field at which the coordinate of the cavity cation becomes 0.25. Thus we *expected discontinuities for the* I- and Br-bearing sodalites but not for the Cl-end member. When the I-end member did not show a discontinuity we did not continue the study with the remaining two aluminogermanate-sodalites. We also expected the sodalite $Sr_8(Al_{12}O_{24})(CrO_4)_2$ to have a discontinuity and were uncertain as to whether $Sr_2Ba_6(Al_{12}O_{24})(SO_4)_2$ would show a discontinuity or not; neither showed a discontinuity.

The absence of discontinuities is most likely related to the much lower expansion coefficients of the aluminate- and aluminogermanate-sodalites compared with the aluminosilicate-sodalites (figure 3). Thus the former structures, because of their low expansion rates, are unable to achieve a state where the coordinate of the cavity cation becomes 0.25 in the temperature ranges investigated. The reason for the lower mean expansion coefficient compared with the aluminosilicate-sodalites is obscure. The calculations leading to figure 7 of Henderson and Taylor (1978) were repeated for frameworks with Al, Si-O and Al, Ge-O bonds. The mean expansion coefficients calculated in this way are shown in figure 4 plotted against the tilt angle, ϕ. According to this figure and the assumptions made one would expect similar expansion coefficients for aluminosilicate- and aluminogermanate-sodalites in similar states of structural collapse. The similar calculated expansion coefficients for $Na_8(Al_6Si_6O_{24})I_2$ (Do, figure 4) and $Na_8(Al_6Ge_6O_{24})I_2$ (D ●, figure 4) are particularly puzzling bearing in mind that the measured expansion coefficient for the former phase is significantly larger than that for the latter (figure 3). Our earlier concept of the mechanism of thermal expansion of the sodalite structure was the expansion of the cavity cation-anion ($\underline{C}$-$\underline{A}$) bond forcing the cavity cation against and between the framework oxygens and untwisting the partially-collapsed structure (Henderson and Taylor, 1978). If this is correct the lower expansion coefficient for $Na_8(Al_6Ge_6O_{24})I_2$ implies that the Na-I bond in this sodalite has a lower expansion coefficient than in $Na_8(Al_6Si_6O_{24})I_2$. However, it now seems likely that our earlier concept was too simple and it is appropriate to consider it further.

The room temperature cell edge of $Na_8(Al_6Si_6O_{24})I_2$ is 9.008 Å and it can be deduced from figure 5 of Henderson and Taylor (1978) that the cell edge at the discontinuity (i.e. the point at which the coordinate of the cavity cation becomes 0.25) should be ~9.33Å. However, the measured cell edge at the discontinuity is only 9.168Å; the difference of 0.16Å can be accounted for by the apparent shortening of the $\underline{T}$-O distance (~2% at the discontinuity (Henderson and Taylor, 1978)) because of anisotropic thermal motion of the framework oxygens. Apparent cavity cation and anion radii were also calculated by Henderson and Taylor (1978) and the resultant apparent $\underline{C}$-$\underline{A}$ bond lengths were shown in their figure 6. These values imply an expansion of the Na-I bond by ~25% between 0° and 810°C; in retrospect this value seems to be unreasonably large. Thus the expansion of the sodalite structure may not be caused by expansion of the $\underline{C}$-$\underline{A}$ bond alone. The different expansion rates of $Na_8(Al_6Si_6O_{24})I_2$ and $Na_8(Al_6Ge_6O_{24})I_2$, which contain the same cavity cation and anion, may be caused by fundamental differences in the rate of untwisting of their frameworks which are of different composition. Thus the thermal expansion behaviour of the sodalite group of minerals seems to depend on the nature of the tetrahedral framework cations as well as the cavity cations and anions.

The identification of the mechanism(s) by which the sodalite framework expands is clearly a complex problem and structural data for various sodalite phases at room and elevated temperatures are essential before further progress can be made. We are currently determining the structures of $Na_8(Al_6Si_6O_{24})I_2$, $Li_8(Al_6Si_6O_{24})Cl_2$, and $K_8(Al_6Si_6O_{24})Cl_2$ at room temperature and hope to be able *to extend this work* to higher temperatures.

Acknowledgements. We gratefully acknowledge the supply of specimens by Professor F.A. Hummel and Dr. D.J. Schipper.

REFERENCES

Depmeier (W.), 1977. Personal communication.
Halstead (P.E.) and Moore (A.E.), 1962. J. Appl. Chem. 12, 413-417.
Henderson (C.M.B.) and Taylor (D.), 1975. Trans. Brit. Ceram. Soc., 74, 55-57.
__________________, 1978. Phys. Chem. Min. 2, 337-347.
Saalfeld (H.) and Depmeier (W.), 1972. Kristall u. Technik 7, 229-233.
Taylor (D.), 1968. Mineral. Mag. 36, 761-769.
__________, 1972. Mineral. Mag. 38, 593-602.
__________ and Henderson (C.M.B.), 1978. Phys. Chem. Min. 2, 325-336.