

Thermal decomposition of $\text{Li}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$

$\text{Li}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$, a synthetic member of the sodalite family (Henderson and Taylor, 1977), was prepared by heating natural sodalite, $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$ (from Låven, Norway), in molten LiCl at 800°C for 2h, washing uncombined LiCl from the product and drying at 110°C. Chemical analyses of the natural sodalite and the Li-sodalite are given in Table 1. The cell edge of the Li-sodalite was 8.4476(9) Å (Si as internal standard: $a = 5.43065$ Å at 25°C) in good agreement with literature values (Henderson and Taylor, 1977).

Simultaneous TG and DTA analyses were car-

ried out on the Li-sodalite by British Ceramic Research Ltd. using a Linseis thermal analyser (experimental conditions: sample weight 102 mg, heating rate 10°C/min in static air, corundum as reference). The DTA curve (Fig. 1) shows three endothermic peaks; the second at 914°C occurs at the start of the weight loss, whilst the third occurs at 1104°C at the point of maximum weight loss (9.4×10^{-3} mg/s). Samples of Li-sodalite were heated in crimped platinum tubes to 950 and 1150°C at a heating rate of 30°C/min. No weight loss was observed after the 950°C heating exper-

TABLE 1. Chemical analyses of: natural sodalite (A), Li-sodalite (B), the theoretical composition of Li-sodalite (C), the thermal decomposition product of Li-sodalite (D), the theoretical composition of LiAlSiO_4 (E), and the theoretical composition of $\text{Li}_8\text{Al}_6\text{Si}_6\text{O}_{25}$ (F).

	(A) [†] wt. %	(B) [*] wt. %	(C) wt. %	(D) [*] wt. %	(E) wt. %	(F) wt. %
SiO ₂	36.6	41.7	42.88	46.8	47.69	45.87
TiO ₂	0.08	<0.01		<0.01		
Al ₂ O ₃	30.3	34.9	36.38	38.9	40.46	38.92
Fe ₂ O ₃	0.38	0.46		0.59		
MgO	0.09	0.13		0.19		
CaO	0.54	0.04		0.05		
Li ₂ O		13.9	14.21	12.6	11.86	15.21
Na ₂ O	24.7	0.11		0.13		
K ₂ O	0.03	<0.01		<0.01		
SO ₃	<0.01					
Cl	6.69	8.34 [†]	8.43	<0.05		
P ₂ O ₅		0.49		0.55		
Mn ₃ O ₄		0.04		0.05		
Loss (800°C)	1.28	0.50 [†]		0.34 ^{**}		
Total	100.69	100.63	101.90	100.20	100.00	100.00
Less O = Cl	1.51	1.88	1.90			
	99.18	98.75	100.00			

[†] Analysed by H.B. Dixon, Fairey Tecramics; ^{*} analysed by British Ceramic Research Limited; ^{**} loss on ignition at 1025°C.

TABLE 2. Cell parameters of beta-eucryptite obtained from the products of the decomposition of Li-sodalite at 950°C (1) and 1150°C (2), and for pure beta-LiAlSiO₄ (3) after Pillars and Peacor (1973).

	a, Å	c, Å	V, Å ³	c/a
1.	10.495(1)	11.204(2)	1068.8(3)	1.0675
2.	10.500(2)	11.205(5)	1069.9(5)	1.0671
3.	10.497(3)	11.200(5)	1068.8	1.0669

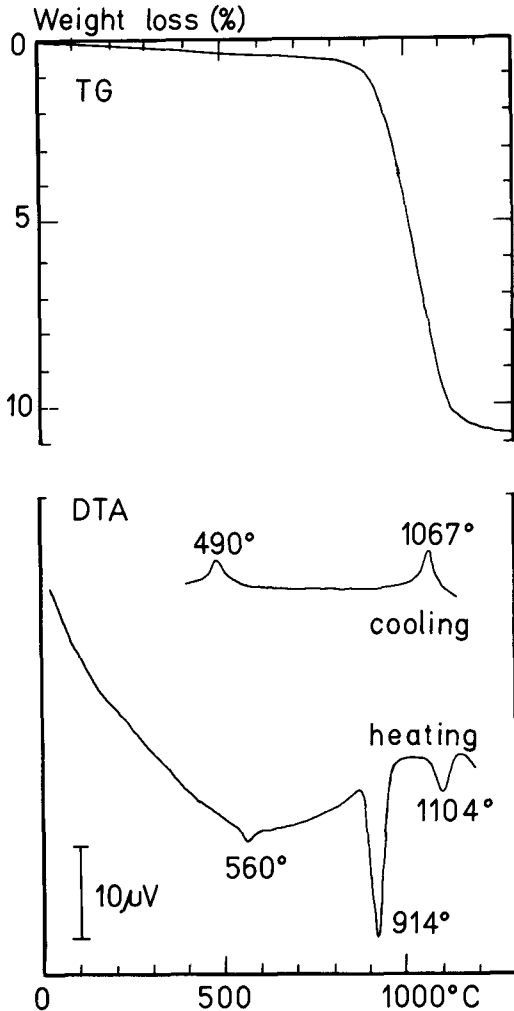


FIG. 1. Thermogravimetric and DTA curves for Li-sodalite.

iment, but a 10.8% weight loss was observed after the 1150°C treatment. Powder X-ray diffraction patterns showed both products to be beta-eucryptite, ideal formula LiAlSiO_4 . The hexagonal cell parameters, calculated by the method of least squares from 9 reflections in the range 34 to 75° 2θ Cu-K α are given in Table 2. The cell parameters are virtually identical and are in good agreement with literature data for pure beta-LiAlSiO₄ (Pillars and Peacor, 1973). The TG curve (Fig. 1) shows that weight loss begins at 880°C and is complete by 1125°C. The loss between 850 and 1150°C was calculated to be 9.9 wt. %.

A 4.0 g sample of Li-sodalite was heated at 30°C/min to 1150°C and had a weight loss of

10.0%. The chemical analysis of the product, beta-eucryptite, is given in Table 1.

The endotherm at 914°C on heating is attributed to the reconstructive transformation of Li-sodalite to beta-eucryptite (the transformation of hydroxysodalite to carnegieite is accompanied by an endotherm at 740°C, Schipper *et al.*, 1973). The endotherm at 1104°C on heating and the exotherm at 1067°C on cooling are assumed to be due to eutectic melting of the impure beta-eucryptite formed from the Li-sodalite. The difference between the two temperatures is most likely due to a slight change in composition (e.g. loss of further LiCl) during the time the temperature was taken to 1300°C. Note that a eutectic at 1070°C has been reported on the Li-rich side of beta-eucryptite in the system Li_2SiO_3 -LiAlSiO₄ (Murthy and Hummel, 1954). The exotherm at 490°C on cooling is attributed to a displacive transformation to a structure of lower symmetry, which is accompanied by the appearance of superstructure reflections (Schultz, 1974).

Loss of chlorine as LiCl from $\text{Li}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$ would give a theoretical weight loss of 10.1%, whereas reaction involving loss of chlorine and incorporation of oxygen (to maintain charge balance) would give a theoretical weight loss of 6.5%. Comparison of analyses (D), (E), and (F) in Table 1 and the weight loss data support the view that $\text{Li}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$ decomposes by incongruent volatilization to beta-eucryptite and LiCl vapour. Natural sodalite also decomposes by incongruent volatilization at high temperatures to nepheline or carnegieite and NaCl vapour (Wellman, 1969). Hydroxysodalite decomposes to carnegieite above 680°C (Schipper *et al.*, 1973). Other halide-bearing aluminosilicate-sodalites have been found to decompose at high temperatures in the vacuum of a powder X-ray diffraction furnace (Henderson and Taylor, 1978), probably by a similar mechanism.

References

- Henderson, C. M. B., and Taylor, D. (1977) *Acta Spectrochim. Acta*, **33A**, 283-90.
- (1978) *Phys. Chem. Minerals*, **2**, 337-47.
- Murthy, M. K., and Hummel, F. A. (1954) *J. Am. Ceram. Soc.* **37**, 14-7.
- Pillars, W. W., and Peacor, D. R. (1973) *Am. Mineral.* **58**, 681-90.
- Schipper, D. J., Lathouwers, T. W., and van Doorn, C. Z. (1973) *J. Am. Ceram. Soc.* **56**, 523-5.
- Schultz, H. (1974) *Ibid.* **57**, 313-8.

Wellman, T. R. (1969) *Geochim. Cosmochim. Acta*, 33, 1302–4. [Manuscript received 3 May 1988; revised 23 June 1988]

© Copyright the Mineralogical Society

KEYWORDS: Li-sodalite, $\text{Li}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$, DTA, TG, decomposition.

Fairey Tecramics Limited, Filleybrooks, Stone, Staffordshire, ST15 0PU.

D. TAYLOR

MINERALOGICAL MAGAZINE, JUNE 1989, VOL. 53, PP. 382–385

A calcian analcime–bytownite intergrowth in basalt, from Skye, Scotland, and calcian analcime relationships

WITHIN a reyerite–tobermorite (11 Å) amygdale assemblage in olivine basalt blocks, near Drynock, Skye, is a porcellaneous material which either lines or completely fills the amygdalae (Livingstone, 1988). Electron-probe microanalysis combined with back-scattered electron imaging identifies individual components of the porcellaneous material as calcian analcime and bytownite, (An_{74-79}). Back-scattered electron imaging reveals a second generation analcime pervading the calcian analcime–bytownite intergrowth and forming patches and discrete veinlets (Fig. 1A).

Chemistry. Ten electron-probe microanalyses of calcian analcime and eight of bytownite are presented in Table 1 as determined on a Cameca Camibax microprobe. Standards utilised were rutile, iron, manganese, jadeite, corundum, and wollastonite at 20 kV and 20 nA. Considerable variation in analcime Na:Ca ratios is apparent, whereas most Si:Al ratios are close to 2:1.

Analyses 2, 5 and 7 possess balance error values, $E(\%)$ (Gottardi and Galli, 1985) of less than 5%, whereas the remaining analyses are greater than 10%. Although the latter are generally unacceptable they are included to present the general picture since this intergrowth material is difficult to analyse:

$$[E\% = 100 \{(\text{Al} + \text{Fe}) - (\text{Na} + \text{K}) - 2(\text{Mg} + \text{Ca})\} / \{(\text{Na} + \text{K}) + 2(\text{Mg} + \text{Ca})\}].$$

In the infrared O–H stretching region analcime (ss) from a phonolite (RMS GY 450.3) displays two maxima at *c.* 3620 and 3550 cm^{-1} , features noted by Oinuma and Hayashi (1967) and other authors. Within the analcime–bytownite intergrowth (hereafter referred to as intergrowth analcime) analcime exhibits a broad absorption with a featureless maximum at *c.* 3420 cm^{-1} (Fig. 2). Sharp absorptions in the O–H region are a characteristic feature of wairakite (Harada *et al.*, 1972).

Wairakite water loss occurs in two distinct stages, at 360 and 500 °C (Gottardi and Galli, 1985), the losses being assigned to two symmetrically independent sites within the structure. Magnesian analcime ('doranite') with only 3 wt.% MgO also exhibits two distinct water losses, at 350 and 430 °C (Dyer *et al.*, 1987, Fig. 3). In marked contrast to wairakite and 'doranite', intergrowth analcime thermal analysis reveals only one water loss (TG 438 °C and DSC 413 °C) with 4.82 wt.% water being expelled. Synthetic Na homoionic analcime loses water at 370 °C (Dyer, pers. comm.) which concurs with DTA and TGA water loss temperatures of 340–370 °C for natural analcime. Differential scanning calorimetry indicates that the intergrowth analcime, with $\Delta H = 99 \text{ Jg}^{-1}$ for water loss, is not a physical mixture of calcian analcime and analcime (ss) since a synthetic Na analcime has $\Delta H = 403 \text{ Jg}^{-1}$. The limit of detection of Na analcime (ss) in the intergrowth, by this method, is approximately 0.1 wt.% (Dyer, pers. comm.).

Point counting on back-scattered electron image photographs indicates intergrowth analcime forms approximately 49% by volume, or 44 wt.%, assuming an S.G. of 2.22 gm cm^{-3} . It follows that intergrowth analcime contains 10.95 wt.% H_2O^+ , a slightly higher than normal value. Cation:water ratios range from 1:1.5 to 2, averaging 1.75.

Significantly, the single water loss at a higher temperature indicates intergrowth analcime is closer to cubic rather than monoclinic symmetry. The intergrowth calcian analcime (60% Na–40% Ca) is thus an intermediate member of a Na analcime–'synthetic Ca analcime' series.

Discussion. From cell parameter data appropriate to the analcime–wairakite series Harada and Sudo (1976) predicted the existence of a monoclinic sodium analogue of wairakite. Additionally,