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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,

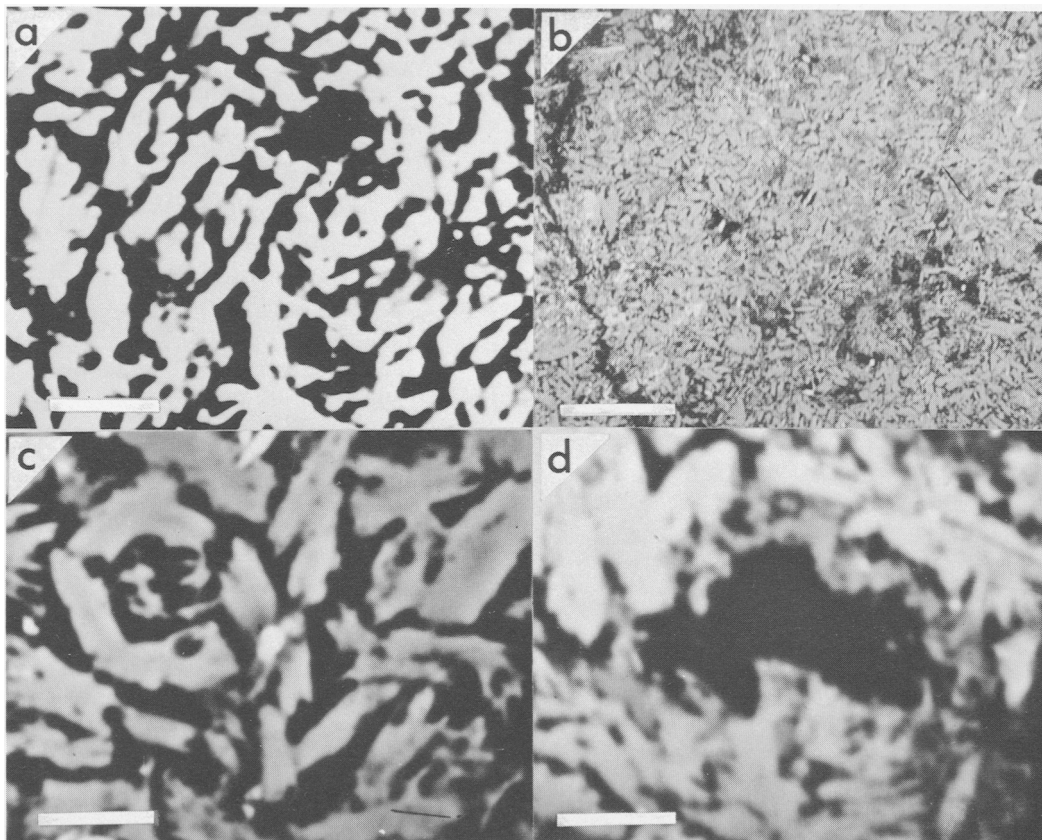


Fig. 1. Back-scattered electron images of porcellaneous material. (a) Intergrowth, showing light areas of calcian analcime-bytownite pervaded by patches, and a vein of sodium-rich analcime (dark areas). Scale bar $100\ \mu\text{m}$. (b) Dark areas are sodium-rich analcime, grey is calcian analcime and white bytownite. Scale bar $10\ \mu\text{m}$. (c) and (d) High-contrast images revealing textural relationships; white bytownite and black calcian analcime. Scale bar $10\ \mu\text{m}$.

their work suggests that analcime (ss) may sometimes possess a $90^\circ 10'\beta$ angle. Mazzi and Galli (1978) wrote of every analcime being different, the primary cause attributable to aluminium ordering.

From X-ray powder diffraction photographs (Fe radiation) analcime line splitting cannot positively be ascertained even though bytownite lines are readily distinguishable. Intergrowth analcime, therefore, was indexed as cubic ($13.692\ \text{\AA}$) although tetragonal and orthorhombic solutions are possible. Takeuchi *et al.* (1979) determined the structure of wairakite ($\beta 90.5^\circ$) and concluded that Ca atoms are fixed to only one site, whereas the small number of Na atoms are evenly distributed over the cation sites. With decreasing calcium content Takauchi *et al.* (1979) concluded that the monoclinic features of the framework will

be gradually lost and cease at a composition of $\text{Ca}/(\text{Ca} + \text{Na})$ ratio of $1/3$. Seven analyses in Table 1 indicate a close approach to this composition with cation : H_2O ratios, suggesting a mixed cation form tending towards a $1:2$ ratio. Indeed, four analyses are very close to this ratio. Seki (1968) erected three legitimate conditions for the X-ray identification of wairakite and concluded that most *synthesised* wairakites reported in the literature were not monoclinic but pseudocubic or tetragonal, i.e. synthetic calcium analcime.

If a zeolite phase of analcime framework was homoionic with respect to calcium then only one water loss peak, at a higher temperature than that of the sodium form, would be expected. The thermal behaviour of intergrowth analcime conforms to this definite parameter for analcime as opposed to either intermediate members or wairakite.

TABLE 1

Electronprobe - microanalyses of intergrowth calcian analcimes and plagioclase.

Calcian analcime										
	1	2	3	4	5	6	7	8	9	10
SiO ₂	56.69	57.33	57.62	57.55	57.12	59.93	58.03	55.49	58.20	51.24
Al ₂ O ₃	24.95	23.08	25.78	23.98	26.95	26.87	25.24	29.31	23.75	28.93
TiO ₂	-	-	0.02	0.02	-	-	0.01	-	0.04	-
FeO	-	-	0.01	0.01	0.03	0.03	-	-	-	-
MnO	0.04	-	-	0.04	0.06	-	0.02	-	-	-
CaO	2.50	0.55	6.83	1.13	8.40	7.24	6.34	6.22	8.53	6.95
MgO	0.02	-	-	-	0.04	-	-	0.02	-	-
Na ₂ O	8.64	12.77	5.74	10.80	6.97	6.62	8.07	5.32	7.88	5.78
	92.84	93.73	96.00	93.53	99.57	100.69	97.71	96.36	98.40	92.90

Structural formulae on basis of 96 oxygens

Si	32.27	32.67	31.84	32.63	30.84	31.68	31.76	30.49	31.88	29.51
Al	16.74	15.50	16.79	16.02	17.15	16.74	16.28	18.98	15.33	19.64
Ti	-	-	0.01	0.01	-	-	-	-	0.02	-
Fe	-	-	-	-	0.01	0.01	-	-	-	-
Mn	0.02	-	-	0.02	0.02	-	0.01	-	-	-
Ca	1.53	0.33	4.04	0.69	4.85	4.10	3.72	3.66	5.01	4.29
Mg	0.01	-	-	0.02	0.03	-	0.02	0.01	-	-
Na	9.53	14.11	6.15	11.87	7.30	6.78	8.57	5.67	8.37	6.44
E%	+32.7	+4.9	+17.9	+20.5	+0.6	+11.7	+1.4	+45.9	-16.6	+30.7
Na+Ca	11.06	14.44	10.19	12.56	12.15	10.88	12.29	9.33	13.38	10.73
Si+Al	49.01	48.17	48.63	48.65	47.99	48.42	48.04	49.47	47.21	49.15
mol's. H ₂ O	20.81	20.82	20.18	20.71	19.74	19.32	19.99	20.08	20.01	21.04
(Na+Ca) :H ₂ O	1.88	1.44	1.98	1.65	1.62	1.77	1.62	2.15	1.49	1.96

Plagioclase

	A	B	C	D	E	F	G	H
SiO ₂	47.83	47.99	48.05	48.03	46.84	47.38	50.70	46.77
Al ₂ O ₃	33.59	33.41	33.48	33.41	33.35	33.21	34.23	33.61
TiO ₂	0.05	0.04	0.04	0.04	0.06	0.01	-	-
FeO	0.04	0.04	-	-	-	0.03	-	-
MnO	0.02	0.02	-	-	-	-	-	-
CaO	15.73	15.15	15.32	15.31	15.67	14.95	14.73	15.82
MgO	0.01	-	0.02	0.02	0.04	0.02	-	-
Na ₂ O	2.34	2.95	2.84	2.71	2.76	2.63	2.50	2.48
	99.61	99.60	99.75	99.52	98.72	98.23	102.16	98.68
An%	78.8	73.9	74.8	75.7	75.8	75.8	76.5	77.8

Analyses 4-6, and E are from central area of specimen shown in F. 1B.

Analysis 4 - from dark centre

5 and 6 from grey calcian analcime intermediate between 4 and bytownite E

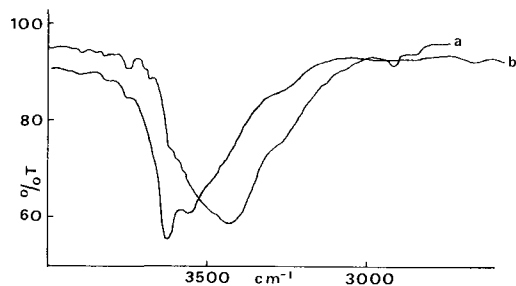


Fig. 2. Infrared scan of O-H stretching region; (a) calcian analcime-bytownite intergrowth; (b) analcime (ss) [RMS GY 450.3].

Apart from the well established analcime-calcian-analcime-wairakite series Takeuchi *et al.* (1979) postulated the existence of a superstructure, or modulated structure, and suggested that if this is the case then the isomorphous series between analcime and wairakite may be extensive. The intergrowth analcime which has a composition of 30-40% Ca/(Ca + Na), may well be an intermediate member in a hereby postulated calcium analogue of analcime-analcime (ss) series. Alternatively, the intergrowth analcime may represent a partially sodium exchanged calcium analogue of analcime as a later Na-rich analcime has clearly pervaded the intergrowth in some areas.

In the Na₂O-Al₂O₃-SiO₂-H₂O system Kim and Burley (1971, 1980) determined an analcime +

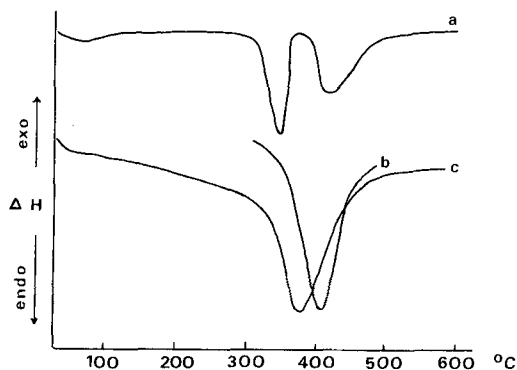


Fig. 3. DSC scan, in static air: (a) 'doranite' with 3% MgO; (b) calcian analcime from intergrowth; and (c) synthetic sodium analcime (a and c at 15°C/min, b at 10°C/min.) After Dyer *et al.* (1987).

albite + vapour field whereas, if CaO is fully substituted for Na₂O in the above system, Liou (1971) ascertained wairakite (+ fluid) formed a separate field from anorthite (+ quartz and fluid). From the co-existence of natural calcian analcime and bytownite it would appear that if Ca and Na are both present in substantial quantities with Al₂O₃-SiO₂-H₂O then, if equilibrium is achieved, Na-Ca analcime-plagioclase assemblages may well form over the whole analcime-'Ca analcime analogue' range with corresponding equilibrium Ab-An compositions.

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Unit cell dimensions of the hydrated aluminium phosphate-sulphate minerals sanjuanite, kribergite, and hotsonite

At the time when the hydrated aluminium phosphate-sulphate hotsonite (Beukes *et al.*, 1984a) and its equally rare relative zaherite (Beukes *et al.*, 1984b; De Bruijn *et al.*, 1985) were discovered near Pofadder, South Africa, very little was known about the unit cells of the other two hydrated aluminium phosphate-sulphate minerals sanjuanite and kribergite, originally described by De Abeledo *et al.* (1968) from Argentin

and to Mr B. Jackson (both of the Department of Geology, Royal Museum of Scotland) for the infrared work. Thanks are also due to Dr. A. Dyer for thermal analysis, permission to use his diagram and critically reading the manuscript. The reyerite and intergrowth phases formed the subject of an enquiry by Sir Fred Stewart and I am grateful to him for permission to work on the material, and providing additional samples from the field.

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and Sweden, respectively. Although the Powder Diffraction file (PDF) contains the X-ray diffraction patterns for sanjuanite and kribergite (PDF 20-47 and 20-48 respectively), they had not been indexed nor have their unit cell parameters been calculated thus far. The purpose of this paper is therefore to index the X-ray power patterns of the latter two minerals and compare their unit cell dimensions with that of hotsonite.