

Some natural analcime solid solutions.

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[Taken as read 8 November 1962.]

Summary. Chemical, optical, and X-ray data are presented on three analcimes from a differentiation sequence, olivine-thermalite to analcime-tinguaitite; compared with the ideal analcime composition, they reveal replacement of NaAl→Si. Optical and X-ray data on these minerals accord reasonably well with analcimes possessing similar compositions, and synthesized in the sub-solidus region in the NaAlSiO₄-NaAlSi₃O₈-H₂O system.

IN recent years considerable data on solid solution relationships in igneous rock-forming minerals has become available, derived either by synthetic investigations or by studies on individual mineral series from differentiation sequences. Except for the data of Saha (1959, 1961), the geochemistry of analcime (NaAlSi₂O₆·H₂O) appears to have received little attention, despite the widespread occurrence of the mineral, often as an essential constituent (e.g. in analcimites and various analcime-alkali-feldspar assemblages) in representatives of alkali olivine-basalt magma. Analcime may also figure as a major component in sedimentary sequences (Van Houten, 1960), or as a product of low grade zeolite facies metamorphism of rocks of appropriate composition (Coombs *et al.*, 1959).

During phase-equilibria studies in the sub-solidus region in the system NaAlSiO₄ (nepheline)-NaAlSi₃O₈ (albite)-H₂O, Saha found analcime as an important phase crystallizing from glasses ranging in composition from NaAlSiO₄, through Na₂Al₂Si₃O₁₀ (anhydrous natrolite) and NaAlSi₂O₆, to NaAlSi₃O₈. For these synthetic analcimes, the following relationships were found: The value $2\theta_{\text{An}(639)} - 2\theta_{\text{Si}(331)}$ (Cu-K α_1) increases with an increase in the molecular ratio $2\text{SiO}_2/(\text{Na}_2\text{O} + \text{Al}_2\text{O}_3)$; and unit-cell dimensions and refractive indices decrease with an increase in this ratio. For natural analcimes, Saha plotted the mol. ratios of silica and water (relative to the arithmetic mean of the number of Al atoms and (2Ca+Na+K) atoms as unity), and related them to a curve based on variation in the molecular ratios of SiO₂ and H₂O for synthetic analcimes. He commented on the more

restricted compositional range of natural analcimes, compared with the synthetic varieties. The majority of natural analcimes studied by Saha plotted close to a constant $\text{SiO}_2:\text{H}_2\text{O}$ molecular ratio of 4:2 and extended to SiO_2 -rich varieties, described from sediments by Ross (1928) (fig. 1, 3).

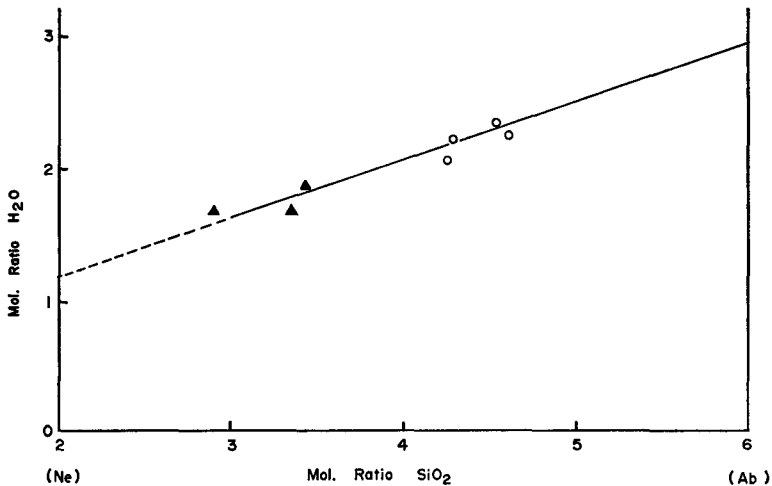


FIG. 1. The Square Top and other analcimes, showing their relation to Saha's curve relating the water content and silica content of synthetic and natural analcimes.

▲ Square Top; ○ Yoder and Weir, 1960.

As a comparatively *minor* component of igneous assemblages, analcime is typically late in the crystallization sequence. Consideration of this fact, together with the fact that analcime possesses a lower temperature stability field than nepheline under low to moderate water vapour pressures, suggests that low-silica-high-alumina analcimes should be developed in igneous assemblages where analcime coexists with nepheline, and where it crystallizes later than the nepheline from potentially Ne-bearing solutions. Moreover, the comparatively high crystallization temperatures of undersaturated alkaline basic rocks (with $\text{Na}_2\text{O} > \text{K}_2\text{O}$) would favour $\text{NaAl} \rightarrow \text{Si}$ replacement within analcime.

Analcimes from the Square Top intrusion.

The above conditions have been realized in the Square Top intrusion (Benson, 1913), west of Nundle, New South Wales, where a continuous

sequence, 250–300 ft thick, reveals the passage of olivine-theralite to analcime-tinguaite. Table I lists analyses of three analcimes in ascending sequence from the lower contacts of the intrusion. Analcimes I

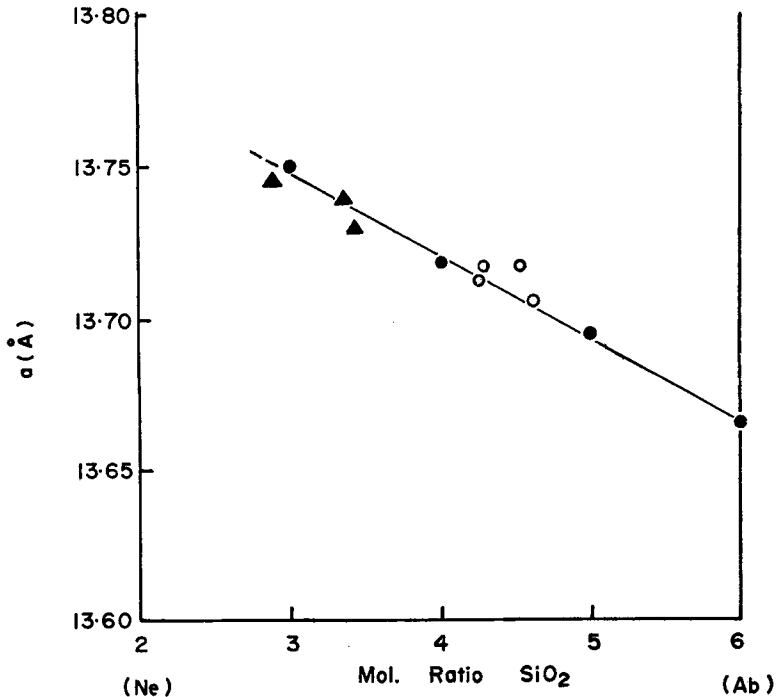


FIG. 2. Variation of the cell dimensions of synthetic and natural analcimes with composition. ▲ Square Top; ○ Yoder and Weir, 1960; ● Synthetic (Saha, 1961).

and II are generally intersertal to plagioclase, alkali feldspar, or nepheline, the latter minerals showing little or no analcimization. Analcime III, from an analcime-tinguaite, porphyritic in nepheline and diopsidic clinopyroxene, occurs interstitially to the alkali feldspar laths of the groundmass. The analcimes were separated from rock crushes by repeated centrifuging in bromoform-alcohol solutions and by treatment on a Frantz Isodynamic separator. Analcimes I and II were recovered 95–97 % pure, the impurities being principally natrolite and minor apatite fibre inclusions. In the case of analcime III, it was not found possible to eliminate composite analcime-alkali-feldspar fragments, and an acid extraction method, similar to that employed in analysis

of nepheline concentrates, was resorted to, treating the analcime concentrate initially with 10 % HCl. Natrolite, with α 1.481, β 1.484, γ 1.493 (identity confirmed by X-ray powder data), may comprise up to 5 % of the mode of theralites and tinguaite, generally as late stage

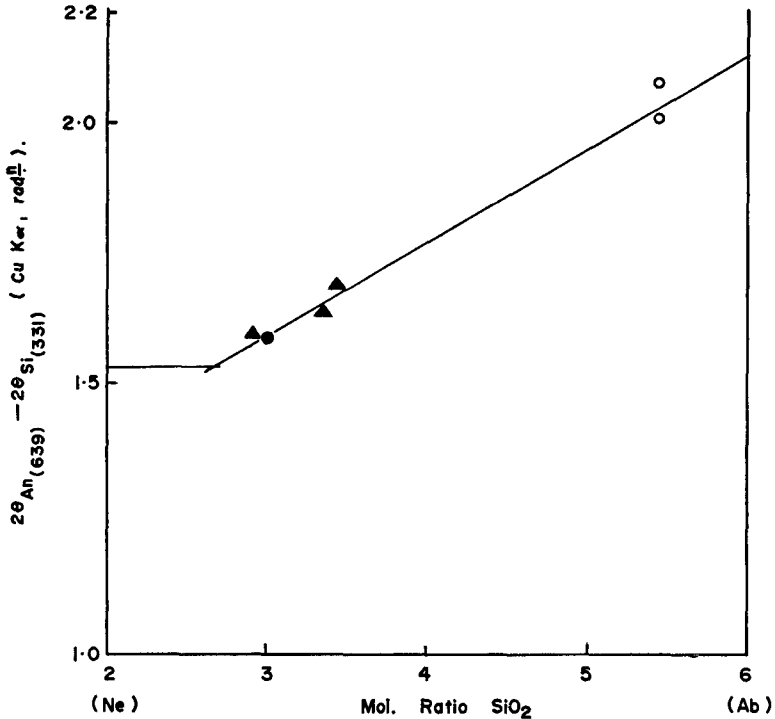


FIG. 3. Curve relating the displacement of the 639 analcime peak with composition. \blacktriangle Square Top; \circ Sedimentary (Ross, 1928; Saha, 1961); \bullet synthesized from natrolite (Saha, 1961).

circular infillings, where it may be associated with analcime. The latter mineral is often idiomorphic against the natrolite. In some tinguaite from the upper levels of the intrusion, the natrolite comprises 20 volume per cent of the rock, and may then replace nepheline.

Crystals of analcimes I and II are clear, transparent, and isotropic; analcime III exhibits slight turbidity. The respective refractive indices are: I, $n = 1.493$; II, $n = 1.490$; III, $n = 1.490 (\pm 0.002)$. These values agree fairly well with the refractive indices of synthetic analcimes

of similar composition, and are higher than those values generally recorded for the natural mineral (i.e. $n = 1.485-1.488$). However, increased refractive indices of the Square Top analcimes may have resulted in part from the entry of small amounts of Ca and Fe into the structure.

The formulae of the three analysed analcimes, calculated on the assumption that the number of oxygens in the unit cell remains ideally constant at 96 (table I), are:

- I. $(\text{Na}_{17.16} \text{Ca}_{0.90} \text{K}_{0.56}) (\text{Al}_{18.97} \text{Fe}_{0.59}^{3+} \text{Si}_{28.45}) \text{O}_{96} \cdot 16.53 \text{H}_2\text{O}$.
 II. $(\text{Na}_{16.05} \text{Ca}_{0.42} \text{K}_{0.56}) (\text{Al}_{17.52} \text{Fe}_{0.70}^{3+} \text{Si}_{29.97}) \text{O}_{96} \cdot 15.15 \text{H}_2\text{O}$.
 III. $(\text{Na}_{16.41} \text{K}_{0.38}) (\text{Al}_{17.73} \text{Fe}_{0.57}^{3+} \text{Si}_{30.08}) \text{O}_{96} \cdot 16.60 \text{H}_2\text{O}$.

For purposes of comparison with Saha's data (figs. 1-3), the molecular ratios of silica and water of the Square Top analcimes have been calculated relative to the arithmetic mean of the number of Al atoms and $(2\text{Ca} + \text{Na} + \text{K})$ atoms as unity. Calculated in this way, the respective $(\text{SiO}_2:\text{H}_2\text{O})$ ratios are: analcime I, 2.91:1.70; II, 3.36:1.70; III, 3.43:1.90. The analcime sequence I→III represents a sequence of differentiation with decreasing temperature. The principal substitution is $\text{NaAl} \rightarrow \text{Si}$, analcime I approximating in its chemistry to natrolite (table I). Although small amounts of Ca are the result of apatite fibre impurities, the bulk of the Ca is probably replacing Na. The amounts of Ca in the analcimes decrease with decreasing temperature, as Ca decreased in the parent rocks. The $(\text{Na} + \text{Ca} + \text{K})$ groups decrease slightly with differentiation, trending towards values more appropriate to the ideal analcime composition. The $\text{H}_2\text{O} +$ values of analcimes I and III are slightly higher than might be anticipated from the bulk chemistry of minerals falling close to the ideal general formulae proposed by Saha (1959) on a basis of water contents of synthetic analcimes, namely 16 $(\text{Na}_{1.2} \text{Al}_{1.2} \text{Si}_{1.8} \text{O}_6 \cdot 0.90 \text{H}_2\text{O})$ (analcime of natrolite composition) to 16 $(\text{Na}_{1.0} \text{Al}_{1.0} \text{Si}_{2.0} \text{O}_6 \cdot 1.0 \text{H}_2\text{O})$ (ideal analcime composition). The analcime compositions plot close to Saha's curve linking variation in water content with variation in silica (fig. 1).

X-ray powder photos of the analysed analcimes yield patterns with thin well-defined lines, with spacings consistent with cubic symmetry and a body-centred unit cell. Line intensities and d -spacings are closely similar to the data listed by Coombs (1955). High angle back reflections of analcime I yielded the unit-cell dimension, $a = 13.753 \pm 0.005 \text{ \AA}$ (Cu- $K\alpha$ radiation). Back reflections of analcimes II and III are diffuse. Hence the unit-cell dimensions of the three analcimes

TABLE I. Analyses of analcimes from the Square Top intrusion, near Nundle, New South Wales.

	I.	II.	III.	A.	B.	C.	I. II. III.				
							Atomic ratios per 96 oxygen.				
SiO ₂ ...	47.23	50.72	50.51	54.58	56.05	47.33	Si	...	28.45	29.97	30.08
Al ₂ O ₃	26.72	25.17	25.27	23.16	22.36	27.13	Al	...	18.97	17.52	17.73
Fe ₂ O ₃ *	1.29	1.56	1.26	0.03	0.03		Fe ³⁺	...	0.59	0.70	0.57
MgO	n.d.	n.d.	nil		0.02		Ca	...	0.90	0.42	—
CaO...	1.40	0.67	tr.		0.00	0.10	Na	...	17.16	16.05	16.41
Na ₂ O	14.70	14.02	14.22	14.08	13.44	15.63	K	...	0.56	0.56	0.38
K ₂ O...	0.73	0.74	0.50		0.10		(Si+Al)	...	47.42	47.49	47.81
H ₂ O+	8.23	7.69	8.36	8.18	8.13	9.54	(Na+Ca+K)	...	18.62	17.03	16.79
H ₂ O-	0.17	0.10	0.05		0.01	0.13	H ₂ O	...	16.53	15.15	16.60
Total	100.47	100.67	100.17	100.00	100.15	99.86					

I. Analcime from olivine-theralite close to lower contact, Square Top.

II. Analcime from leucocratic olivine-theralite, approximately 70 ft above I, Square Top.

III. Analcime-tinguaite, from exposed top of intrusion, Square Top.

A. Ideal composition of analcime (NaAlSi₂O₆·H₂O).

B. Analcime (slightly SiO₂-rich), Golden, Colorado (Yoder and Weir, 1960). (Includes TiO₂ 0.01%.)

C. Natrolite from nepheline-syenite, Wykertown, New Jersey (Milton and Davidson, 1950).

(Analyses I and II by J. Pyle, Department of Mines, Sydney, and by Japan Analytical Chemistry Research Institute. Analysis III by J. Pyle.)

* Total iron as Fe₂O₃.

were measured from the analcime 10.5.5 reflection¹ on a Philips diffractometer, using the 311 and 312 reflections of quartz ($2\theta = 83.84^\circ$ and $2\theta = 90.83^\circ$, respectively, for Cu- $K\alpha_1$) as internal standards. The respective unit cell dimensions are: analcime I, a 13.744; II, a 13.739; III, a 13.730 (± 0.005 Å). These values are higher than the cell dimensions usually recorded for natural analcimes, namely a 13.70–13.72 Å. In fig. 2, the unit cell dimensions for the synthetic analcimes are those listed by Saha (1961) for Cu- $K\alpha_1$ radiation. Yoder and Weir (1960) obtained values of a 13.705–13.717 Å (Cu- $K\alpha_1$) on natural analcimes possessing a slight excess of SiO₂ (up to 2.48 weight per cent) over the ideal composition (table I).

Measurement of the 639 analcime peak against the 331 peak of silicon ($2\theta = 76.37^\circ$) as internal standard also indicates the SiO₂-poor nature of the Square Top analcimes (fig. 3). The value $2\theta_{\text{An}(639)} - 2\theta_{\text{Si}(331)}$ for analcime I falls close to this value for analcime synthesized from natrolite. Saha (1961) has postulated a break in the curve for the displacement of the 639 analcime peak, approximately at the composition Na₂O.Al₂O₃.2.75 SiO₂.

Discussion.

The Square Top analcimes extend the range of composition of natural analcimes towards low SiO₂ molecular ratios. Their chemical and X-ray data agree reasonably well with the data on synthetic analcimes of similar composition. In the case of analcime I, its highly sodic nature is related to the earlier precipitation of a strongly sodic nepheline (Na₂O = 19.69, K₂O = 1.93 weight per cent). For the parent rock, Na₂O = 5.02, K₂O = 1.72 per cent. Despite parent rock enrichment in K₂O with differentiation (the analcime-tinguaitite has Na₂O = 8.93, K₂O = 4.08 per cent), the analcimes consistently remain potash-poor, K being preferentially incorporated in earlier precipitated nepheline and alkali feldspar. Analcimes coexisting with alkali feldspar only tend to be more potash-rich (Wilkinson, 1962) than analcimes from the Square Top intrusion in which nepheline appears as an earlier phase of crystallization. Excluding alkali feldspar, the generalized crystallization sequence of the alkali alumina silicates in the Square Top rocks is: nepheline → analcime → natrolite (cf. the natrolite- and analcime-bearing tinguaite from north-eastern Uganda, described by Hytönen, 1959). The above sequence accords with natrolite probably possessing the lowest temperature stability field of the three minerals (Sand *et al.*,

¹ This is actually a superposition of 10.5.5, 10.7.1, and 11.5.2; ($h^2 + k^2 + l^2$) = 150.

1957). It is hoped to evaluate the interrelationships between the coexisting plagioclase and alkali feldspars, nepheline, and analcime in the Square Top intrusion.

Acknowledgements. The writer is indebted to Professor D. S. Coombs and Dr. P. Saha for their constructive criticism of the manuscript. The analytical contributions of Mr. J. Pyle are gratefully acknowledged. The work was aided by a research grant from the University of New England.

References.

- BENSON (W. N.), 1913. Proc. Linn. Soc. N.S.W., vol. 38, p. 703.
 COOMBS (D. S.), 1955. Min. Mag., vol. 30, p. 699.
 COOMBS (D. S.), ELLIS (A. J.), FYFE (W. S.), and TAYLOR (A. M.), 1959. Geochimica Acta, vol. 17, p. 53.
 HYTÖNEN (K.), 1959. Bull. Comm. Géol. Finlande, vol. 31, no. 184, p. 75.
 MILTON (C.) and DAVIDSON (N.), 1950. Amer. Min., vol. 35, p. 500.
 ROSS (C. S.), 1928. Ibid., vol. 13, p. 195.
 SAHA (P.), 1959. Ibid., vol. 44, p. 300.
 ——— 1961. Ibid., vol. 46, p. 859.
 SAND (L. B.), ROY (R.), and OSBORN (E. F.), 1957. Econ. Geol., vol. 52, p. 169.
 VAN HOUTEN (F. B.), 1960. Journ. Geol., vol. 68, p. 666.
 WILKINSON (J. F. G.), 1962. Journ. Petrology, vol. 3, p. 192.
 YODER (H. S.) and WEIR (C. E.), 1960. Amer. Journ. Sci., vol. 258-A (Bradley vol.), p. 420.
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