

GEOCHEMICAL AND X-RAY INVESTIGATION OF NATURAL AND SYNTHETIC ANALCITES*

PRASENJIT SAHA, *The Pennsylvania State University
University Park, Pennsylvania.*

ABSTRACT

During phase-equilibria studies in the subsolidus region of the system NaAlSiO_4 (nepheline)- $\text{NaAlSi}_3\text{O}_8$ (albite)- H_2O , analcite was synthesized from glasses of a wide range of composition. Geochemical, optical, and x-ray investigations were carried out and it was found that there is a wide range of solid solution of analcite. Determination of water content and unit cell constant proved that the variation of these properties are linear functions of the silica content of the analcites. The synthetic analcites were found to be isotropic, but the refractive index variation was not found to be linear. The experimental data have been discussed in the light of previous structural investigations of analcites. Data on the composition of natural analcites have been collected from literature and summarized.

INTRODUCTION

During a study of the phase equilibrium relations in the system $\text{NaAlSi}_3\text{O}_8$ - NaAlSiO_4 - H_2O analcite was synthesized from glasses ranging in composition from NaAlSiO_4 to $\text{NaAlSi}_3\text{O}_8$. The present paper deals with some optical and powder diffraction studies of the synthetic and some natural analcites. Data from the literature have also been collected and summarized.

The structure of analcite ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$) has been worked out by W. H. Taylor (1930, 1938). It is a zeolite, the main structural feature being the presence of diagonal channels surrounded by six-fold rings of silica tetrahedra; the channels do not cross each other. The water molecules are situated inside these channels. The sodium atoms are surrounded by four-fold rings of silica tetrahedra. The structure is apparently cubic, and the lattice constant has been determined to be 13.7 Å (Bragg, 1937), but some variation has been reported (Grüner, 1928). The space group has been determined to be $Ia3d(O_h^{10})$, but Grüner suggested that $Im3m(O_h^9)$ is more probable, since he observed some reflections in oscillation photographs which could not be accounted for by the space group $Ia3d$. Schiebold (1930) considered the mineral to be tetragonal, space group $I4/acd(D_{4h}^{20})$. Taylor assumed equivalent positions for Si and Al, assigned the water molecules to a 16-fold special position (0.125, 0.125, 0.125), but assumed that the 16 Na atoms randomly occupied a 24-fold special position (0.125, 0, 0.25). Náray-Szabó (1938) suggested that analcite has the same structure as pollucite, i.e., space group D_{4h}^{20} pseudomorphic after O_h^{10} , and he proposed an alternate arrangement for the Na atoms and the water molecules, the former oc-

* Mineral Industries Contribution No. 58-3.

cupying one 16-fold special position (0.125, 0.125, 0.125) and the latter partially occupying a 24-fold special position (0, 0.25, 0.125).

All these structural investigations were based on the following assumptions: (1) Ideal, stoichiometric composition of analcite was assumed ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$), (2) though x -ray photographs of analcite indicate cubic symmetry, many of the specimens examined show optical anomalies, i.e., weak to moderate birefringence. Hence it has been assumed that the mineral is pseudo-cubic. As Bragg (1937) states, "It is not definitely established that statistically cubic symmetry is brought about by the constant interchange of the Na atoms. Whereas perfect cubic symmetry is impossible with 16 fixed Na atoms distributed among 24-fold positions, Taylor points out that such a distribution is compatible with tetragonal symmetry. It is possible that analcite has an intimate twinning of tetragonal components which simulates cubic symmetry."

Barrer (1950) has shown that the sodium ions in analcite can be readily exchanged by potassium, thallium, and rubidium ions. If Taylor's model of analcite structure is assumed to be correct, it is difficult to explain how these ions can substitute for sodium. The Na-O distance (Beattie, 1954), in the analcite structure, assuming Taylor's model, is 2.6 Å, leaving only 1.2 Å for the cationic radius, if the oxygen is taken to have an ionic radius of 1.4 Å. Thus potassium, thallium, and rubidium ions are too large to fit into the sodium positions. All these ion-exchanged analcites are noncubic at room temperature. Beattie (1954) explained this kind of substitution by assuming that potassium, thallium, and rubidium ions will be repulsed and forced away from the sodium position towards the position normally occupied by caesium in pollucite (0.125, 0.125, 0.125). The potential energy for such an ion will then lie in some position intermediate between that of caesium and that of sodium. The structure will then no longer possess cubic symmetry.

Recently Coombs (1955) obtained some powder data on noncubic analcite. The powder photograph shows distinct evidence of the noncubic nature of the specimen. Coombs has classified analcite into the three following groups: (1) Strictly cubic and isotropic, space group Ia^2d . The synthetic specimen, hydrothermally prepared (Barrer, 1952), appears to belong here, (2) birefringent and biaxial, departures from cubic lattice dimensions not detectable although anomalous x -ray reflections may appear, i.e., Flinders analcime, (3) trigonal or nearly trigonal with rhombohedral angle approximately 90.5° , e.g., Låven analcime. Biaxial specimens from the same locality must be of lower symmetry.

Single crystal work has not been done with the distinctly noncubic Låven specimen.

Guyer, Ineichen, and Guyer (1957) reported the synthesis of analcites

from compositions ranging from $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}$ (anhydrous natrolite) to $\text{NaAlSi}_5\text{O}_{12}$ (anhydrous sodium mordenite). The powder diffraction data presented in the paper show distinct evidence of change in the lattice constant. The unit cell size decreases towards higher silica compositions. They assumed that this is due to the smaller bond distance between silicon and oxygen atoms compared to the Al-O bond distance.

PRESENT WORK

Subsolidus studies in the system $\text{NaAlSi}_3\text{O}_8\text{-NaAlSiO}_4\text{-H}_2\text{O}$ indicate that analcite crystallizes from glasses of composition ranging from NaAlSiO_4 (nepheline) to $\text{NaAlSi}_3\text{O}_8$ (albite). The phase equilibria studies will be discussed in a later paper. The most interesting feature is that analcite is the only phase which crystallizes from glasses of composition ranging from $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}$ (anhydrous natrolite) to $\text{NaAlSi}_3\text{O}_8$ (albite), except for very small quantities of another yet unidentified phase in some runs ($\approx 3\%$, modal analysis). When observed under the microscope, no unreacted glass could be observed in these runs. Since all the runs were made in sealed gold tubes, the analcite crystals synthesized must have the same composition as the glass from which it crystallized, with the addition of water.

Optical Properties of Analcite Solid Solution

The synthetic analcites were found to be isotropic, quite in accord with Barrer's (1952) and Coombs' (1955) observations. The small amount of the other still unidentified phase in some runs has a high refringence and birefringence, and can be readily distinguished from the analcite grains. The refractive index of synthetic analcites of different compositions have been plotted in Fig. 1 and show that the refractive indices decrease with increasing silica content. The limit of error is $\pm .002$.

X-Ray Diffraction Studies of Analcite Solid Solution

The variation in composition of synthetic analcites was confirmed by the change in d -spacings observed in the back reflection region, using silicon as internal standard. The (639) peak of analcite falls at higher angles for analcites of higher silica content. The resolution of the $K\alpha_1$ and $K\alpha_2$ peaks in analcite of albite composition is not so well defined, and this is probably due to imperfect crystallization. The difference $2\theta_{\text{An}(639)} - 2\theta_{\text{Si}(331)}$ ($\text{CuK}\alpha_1$ radiation) has been plotted against variation in SiO_2 content in Fig. 2. The lattice constant " a " was calculated from the change in d -spacing and plotted in Fig. 3. Both Figs. 2 and 3 show that the variations are linear.

Hydrothermal studies on the stability of natrolite showed that only

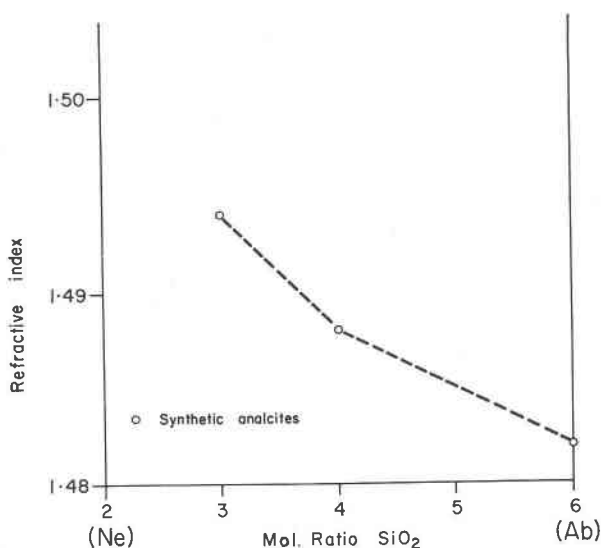


FIG. 1. Refractive index of synthetic analcites.

analcite appeared in glasses of anhydrous natrolite composition ($\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}$). Runs made with natural specimens of natrolite also indicated that natrolite breaks down to analcite. The d -spacing variation of this analcite has been plotted in Fig. 2, and assuming stoichiometric composition of the natrolite, it can be seen that it falls very close to the curve.

Two specimens of analcite from sedimentary rocks (Yavapai County, Arizona) were kindly sent by Dr. C. S. Ross for x-ray diffraction and single crystal studies. These analcites have previously been described by Ross (1928). The crystals are isotropic and the refractive index is 1.483. The $K\alpha_1$ peak is sharp, but the $K\alpha_2$ peak is not so well resolved. However single crystal work shows that there is no deviation from cubic symmetry. In his paper (1928) Dr. Ross gave two analyses. One interesting feature of these analyses is that the water and silica content are in excess of that required for the ideal composition of analcite. There is no appreciable difference in the proportion of silica in the two analyses. The author received two samples of these analcites, but did not know which specimen represented which analysis. The d -spacing variations were plotted assuming the mean of the two analyses. The points fall very close to the curve for the synthetic analcites (Fig. 2). The small differences in the silica contents of the two analyses will not significantly change the position of the points on this graph.

A specimen of analcite occurring as clusters of transparent icositetra-

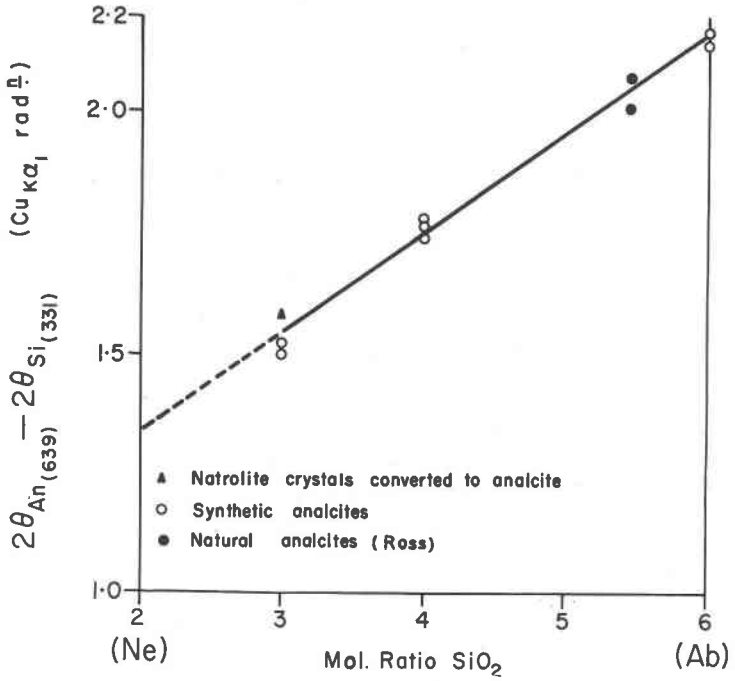


FIG. 2. Variation of $d_{(639)}$ spacing of synthetic and natural analcites with variation of SiO_2 content.

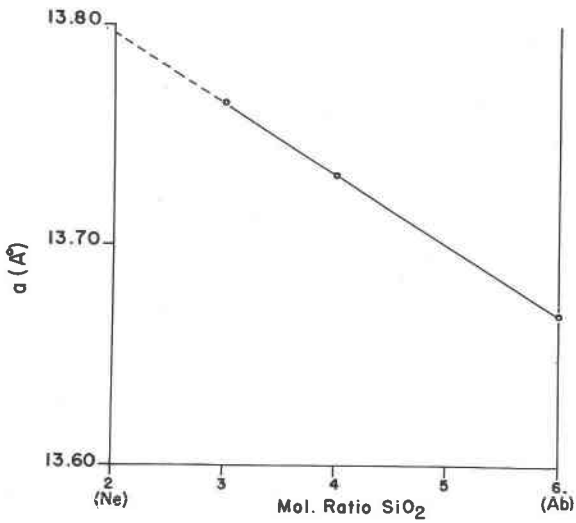


FIG. 3. Variation, with composition, of the lattice parameter of synthetic analcites.

hedral crystals in the cavities of a basaltic rock (Specimen No. 450.2, Patagonia, Sicily) indicates a relatively small shift in the (639) peak compared to the Si internal standard. The mineral is weakly anisotropic, and the refractive index is $1.488 \pm .002$. Single crystal photographs indicate that the specimen is cubic. Though the sample has not yet been analyzed, a deficiency in water and silica is suspected. The main purpose of including this sample in this discussion was to bring out the shifting of the (639) peak for different natural analcites.

The x-ray diffraction pattern of a specimen of analcite from Patterson, New Jersey, which was found to be moderately birefringent gave a very diffuse (639) peak in the back-reflection regions.

Geochemical Studies of Natural Analcites

Data on the variation of chemical composition of analcite were collected from the literature. Sixty-eight analyses were collected from Doelter (1917), and 25 were collected from other papers, summarized in the Mineralogical Abstracts. In the zeolite structure, as in other tectosilicate structures, the charge deficiency caused by the substitution of aluminum ions for silicon ions is compensated by larger cations like calcium, sodium and potassium.* Thus for charge balance, $Al = 2Ca + Na + K$. This assumption was used as a check on the accuracy of the analyses. A deviation of ± 30 atoms was allowed. All the available analyses from the literature have been tabulated in Table 1, and the mol. ratios of silica and water have been calculated, taking the arithmetic mean of the number of Al atoms and $(2Ca + Na + K)$ atoms as unity. On this basis, 59 analyses could be plotted (Fig. 4). One very significant feature is apparent from the diagram, the water content increases with the increase in silica content.

Analyses of Water of Synthetic Analcites

The water content of analcites synthesized from glasses of compositions $Na_2Al_2Si_3O_{10}$, $NaAlSi_2O_6$, and $NaAlSi_3O_8$ were determined by the loss on ignition method. About 50 milligrams of analcites of these compositions were prepared hydrothermally in runs of 1 month duration. The charges were sealed in thick-walled gold tubes with excess water, so that nothing could be carried away in solution. The gold tubes were carefully weighed before and after the synthesis, and since there was no appreciable loss in weight the composition of the charges did not change. After the synthesis, a small portion of the product was observed under the

* Since calcium is divalent, two aluminum ions are required to substitute for two silicon ions when one calcium ion enters the structure. Substitution of one aluminum ion for one silicon ion is required when one sodium or potassium ion enters the structure.

TABLE I. ANALYSES OF ANALCITE

No.	Number of atoms							SiO ₂ :H ₂ O× Mol. ratio	
	Si	Al	H ₂ O	Ca	Na	K	2Ca+Na +K		Δ ⁻
1	918	451	459	—	437	—	437	14	4.1:2.1
2	940	431	489	—	445	—	445	14	4.3:2.2
3	917	436	456	—	442	—	442	6	4.2:2.1
4	854	462	586	—	166	—	166	296*	
5	926	451	438	—	473	—	473	22	4.0:1.9
6	955	443	500	6	383	12	407	36*	
7	918	462	458	—	459	—	459	3	4.0:2.0
8	957	454	444	100	208	—	408	46*	
9	934	471	444	104	208	—	416	55*	
10	915	463	460	—	454	—	454	9	4.0:2.0
11	917	454	453	—	454	—	454	0	4.0:2.0
12	894	452	472	22	256	95	395	57*	
13	919	454	426	5	393	32	435	19	4.1:1.9
14	905	463	450	4	420	14	442	21	4.0:2.0
15	936	436	462	5	390	31	431	5	4.3:2.1
16	944	416	544	—	294	—	294	122*	
17	927	441	488	—	398	—	398	43*	
18	912	453	461	4	419	17	444	9	4.1:2.1
19	913	443	503	16	406	—	438	5	4.2:2.3
20	907	451	460	—	452	—	452	1	4.0:2.0
21	925	437	475	—	444	—	444	7	4.2:2.2
22	929	481	488	—	413	—	413	68*	
23	889	455	501	—	468	3	471	16	3.8:2.2
24	938	432	488	9	426	—	444	12	4.3:2.2
25	893	451	474	7	433	—	447	4	4.0:2.1
26	887	458	470	11	469	—	491	33*	
27 ¹	898	483	472	—	717	28	745	262*	
28	912	464	473	6	436	—	448	16	4.0:2.1
29	906	449	454	30	341	43	444	5	4.1:2.0
30	899	471	465	—	436	—	436	35*	
31 ^a	906	449	451	16	419	—	451	2	4.0:2.0
<i>b</i>	920	416	278	66	288	58	478	62*	
32	950	422	462	—	440	7	447	25	4.4:2.1
33	912	449	462	—	452	—	452	3	4.1:2.1
34	911	454	458	6	397	17	426	28	4.1:2.1
35	929	440	465	—	435	—	435	5	4.2:2.1
36	907	457	453	—	454	—	454	3	4.0:2.0
37	892	472	460	15	439	—	469	3	3.8:2.0
38	894	473	463	8	486	—	502	29	3.7:1.9
39	883	463	444	—	491	—	491	28	3.7:1.9
40	886	486	458	—	472	—	472	14	3.7:1.9
41 ^a	914	457	416	34	336	34	438	19	4.1:1.9
<i>b</i>	830	442	613	47	352	57	503	61*	
42	896	461	450	—	466	—	466	5	3.9:1.9
43 ^a	954	410	509	6	369	—	381	29	4.8:2.6
<i>b</i>	968	401	488	7	369	—	383	18	4.9:2.5
<i>c</i>	973	423	455	6	358	—	370	53*	
<i>d</i>	981	391	492	6	376	—	388	3	5.0:2.5
<i>e</i>	934	425	500	14	369	—	397	28	4.5:2.4
44	919	448	477	—	434	—	434	14	4.2:2.2
45	906	452	470	4	430	4	442	10	4.1:2.1
46	853	471	504	29	375	27	460	11	3.7:2.2
47 ²	950	421	465	3	394	—	400	21	4.6:2.3
48 ²	928	452	458	3	402	—	408	41*	

TABLE 1 (Continued)

No.	Number of atoms								SiO ₂ :H ₂ OX Mol. ratio
	Si	Al	H ₂ O	Ca	Na	K	2Ca+Na +K	Δ ⁻	
49	943	402	516	—	407	—	407	5	4.7:2.6
50	879	424	455	12	477 ⁸	—	501	77*	
51	702	604	696	148	197	—	493	111*	
52	913	475	472	1	387	—	389	87*	
53	906	426	483	24	444	—	492	66*	
54	830	201	791	223	356	21	823	622*	
55	941	430	485	10	367	11	398	32*	
56	936	425	466	6	429	9	450	25	4.3:2.1
57	941	438	481	—	421	—	421	17	4.4:2.2
58	931	440	463	—	417	—	417	23	4.4:2.2
59	906	463	457	—	431	3	434	29	4.1:2.0
60	910	458	470	—	435	—	435	23	4.1:2.1
61	917	448	465	—	425	—	425	23	4.2:2.1
62	940	434	466	—	421	2	423	11	4.4:2.2
63	946	448	459	—	409	5	414	34*	
64	894	450	507	—	460 ⁴	—	460	10	
65	902	464	457	8	432	7	455	9	3.9:2.0
66	899	456	456	31	356	34	452	4	4.0:2.0
67	902	454	455	28	357	34	447	7	4.0:2.0
68 ²	899	484	479	17	324	48	406	78*	
69	904	464	464	—	445	—	445	19	4.0:2.0
70	978	416	466	2	358	2	376	40*	
71	942	438	483	3	385	9	400	38*	
72 ²	856	452	533	21	274	95	411	41*	
73	914	457	417 ⁵	34	337	34	439	18	
74	830	442	614 ⁵	47	352	57	502	60*	
75	941	424	452 ⁶	14	322	47	397	27*	
76	918	449	456	2	445	4	453	4	4.1:2.0
77	926	498	472	2 ⁷	352	3	359	139*	
78	907	463	456	—	435	4	439	24	4.0:2.0
79	1,009	353	464	1	354	21	377	24	5.5:2.5
80	979	351	477	9	316	32	366	15	5.4:2.7
81	957	409	468	9	353	14	385	24	4.8:2.4
82	909	452	483	8	436	—	452	0	4.0:2.1
83	905	428	501	21	377	23	442	14	4.2:2.3
84	881	483	425	3	429	16	451	32*	
85	940	436	482	—	419	—	419	17	4.4:2.3
86a	1,000	388	464	4	374	2	384	4 _s	
b	1,094	334	370	14	305	2	335	1 _j	

Δ⁻ = |Al - (2Ca + Na + K)|.

x—Taking the arithmetic average of the number of Al atoms and the number of (2Ca + Na + K) atoms as unity.

*—Analyses not used for plotting in Fig. 4.

1—Addition of oxides does not give the total stated in the analysis.

2—Only (H₂O+) plotted in the column marked "H₂O." In the other analyses, where only "H₂O" is stated in the analyses, it was assumed that all the water is (H₂O+) water.

3—Na + K.

4—Not plotted in Fig. 4, because wt% Na₂O was assumed to be = 100 - Σ other constituents (SiO₂ + Al₂O₃ + H₂O).

5—(H₂O+) + (H₂O-). Not plotted in Fig. 4.

6—(H₂O+) and (H₂O-) probably interchanged by mistake in the original analysis. Not plotted in Fig. 4.

7—(CaO + SrO).

8—Not plotted because of enclosed grains of quartz.

TABLE 1 (Continued)

No.	Year	Name of analyst	Locality	Association
1	1822	Rose	Fassatal, Tyrol	—
2	1822	Rose	Fassatal, Tyrol	—
3	1829	Connel	Old Kilpatrick, Scotland	—
4	1836	Thomson	Dumbarton, Kilpatrick, Scotland	(weathered, cloudy sp.)
5	1836	Thomson	Giant's Causeway, Ireland	Amygdaloidal basalt
6	1839	Henry	Blagodat Mt., Ural	(with magnetite)
7	1842	Awdejew	Lövö, Norway	—
8	1847	Riegel	Niederkirchen, Bavaria	—
9	1847	Riegel	Niederkirchen, Bavaria	—
10	1850	Bork & Berlin	Låven, Norway	—
11	1850	Bork & Berlin	Låven, Norway	—
12	1853	Sartorius v. Walters- hausen	Cyclopean Islands, Sicily	Volcanic rocks
13	1858	Rammelsberg	Cyclopean Islands, Sicily	—
14	1858	Rammelsberg	Cyclopean Islands, Sicily	—
15	1858	Rammelsberg	Wesseln, Bohemia	—
16	1863	Stromeyer	Duingen, Hannover	Ironstone shale (?)
17	1864	Bischof	Seiseralpe, Tyrol	—
18	1869	Tschermak	Punzau, Silesia	Teschenite
19	1873	Young	Crofthead, Scotland	—
20	1873	Young	Mugdock, Scotland	—
21	1873	Young	Barrhead, Scotland	—
22	1874	Pisani	Brevik, Norway	—
23	1875	Paijkull	Brevik, Norway	—
24	1876	Lemberg	Fassatal, Tyrol	Melaphyre
25	1877	Lemberg	Predazzo, Tyrol	Porphyritic rock
26	1878	Harrington	Montreal, Canada	—
27	1879	Luedecke	Heldburg, Thuringia	In fissures in phonolith
28	1880	Preis	Kuchelbad, Bohemia	In druses in diabase
29	1881	Ricciardi & Speciale	Cyclopean Islands, Sicily	Basalt
30	1881	Damour	Låven, Norway	—
31a	1881	Nikolajew	Blagodat, Ural	(crystalline sp.)
b	1881	Nikolajew	Blagodat, Ural	(massive sp.)
32	1882	Bamberger	Monte Catini, Tuscany	With chalcopyrite in gabbro
33	1883	Lemberg	Låven, Norway	—
34	1884	Sauer	Wiesental, Bohemia	Leucitophyre
35	1885	Cross & Hillebrand	Table Mt., Colorado, U.S.A.	In vesicles in basalt
36	1884	Lorenzen	Kangerdluarsuk, Greenland	—
37	1887	Hersch	Cyclopean Islands, Sicily	—
38	1889	Johnsson	Klein-Arö, Norway	—
39	1889	Langlet	Klein-Arö, Norway	—
40	1889	Brögger	Eikaholmen, Norway	—
41a	1890	Lindgren	Highwoods, Rocky Mt., Montana, U.S.A.	Sandstone
b	1890	Melville	Highwoods, Rocky Mt., Montana, U.S.A.	Sandstone
42	1892	Brauns	Friedensdorf, Hessen	In fissures in diabase
43a	1893	Zschau	Dresden, Saxony	Syenite (colorless sp.)
b	1893	Zschau	Dresden, Saxony	Syenite (red sp.)
c	1893	Zschau	Dresden, Saxony	Syenite (red sp.)
d	1893	Zschau	Dresden, Saxony	Syenite (red sp.)
e	1893	Zschau	Dresden, Saxony	Syenite (colorless sp.)
44	1895	Glinka	Kobi, Persia	Mud volcano
45	1896	Fairbanks	Point Sal, California, U.S.A.	Augite teschenite
46	1895	Hillebrand	Colorado, U.S.A.	Basalt
47	1899	Clarke & Steiger	Wasson's Bluff, Nova Scotia	—
48	1900	Clarke & Steiger	North Table Mt., Colorado, U.S.A.	—
49	1901	Thugutt	Seiseralpe, Tyrol	—
50	1901	Evans	Mt. Girnar, Kathiwar, India	Monchiquite

TABLE 1 (Continued)

No.	Year	Name of analyst	Locality	Association
51	1904	Takimoto	Maze, Echigo, Japan	—
52	1905	Egleson	Montreal, Canada	Nepheline syenite
53	1907	Anderson	Ben Lomond, Australia	—
54	1907	Tsukamoto	Maze, Echigo, Japan	Basalt
55	1908	Baschieri	Seiseralpe, Tyrol	—
56	1907	Manasse	Hamasat, Massaua	Augite teschenite
57	1913	Tschirwinsky & Orloff	Kara-Dagh, Krim	—
58	1912	Foote & Bradley	Two Isles, N.S.	(average of two sp.)
59	1912	Foote & Bradley	Cyclopean Islands, Sicily	(average of two sp.)
60	1912	Foote & Bradley	Kerguelen Islands	(average of two sp.)
61	1912	Foote & Bradley	Victoria, Australia	(average of two sp.)
62	1912	Foote & Bradley	Michigan, U.S.A.	(average of two sp.)
63	1912	Foote & Bradley	Montreal, Canada	(average of two sp.)
64	1928	Curlo	Murlo, Tuscany	—
65	1926	Di Franco	Cyclopean Islands, Sicily	Basalt
66	1929	Grassi-Cristaldi & Scafile	Cyclopean Islands, Sicily	—
67	1929	Grassi-Cristaldi & Scafile	Cyclopean Islands, Sicily	—
68	1928	Hewett, Shannon & Gonyer	Ritter Hot Spring, Grant County, Oregon, U.S.A.	In cavities in vesicular basalt
69	1929	Hodge-Smith	Kyogle, Australia	In vesicles in basalt
70	1939	Kašper	Morcinov, Czechoslovakia (?)	Amygdaloidal melaphyre
71	1933	Kratochvíl	Budnany, Bohemia	Diabase
72	1938	Larsen & Buie	Highwood Mt., U.S.A.	Phenocrysts in analcite basalt
73	1938	Larsen & Buie	Highwood Mt., U.S.A.	Dyke rock
74	1938	Larsen & Buie	Highwood Mt., U.S.A.	Dyke rock
75	1928	Lonsdale	Terlingua, U.S.A.	Altered basalt
76	1945	Morgante	Diredana, Eritrea	Basalt lavas & tuffs
77	1935	Reichert & Erdélyi	Dunabogdany, Ungarn	—
78	1947	Roques	Kassa Island	Nepheline syenite pegmatite
79	1928	Ross	Yavapai, Ariz., U.S.A.	Lake beds & playa deposits
80	1928	Ross	Yavapai, Ariz., U.S.A.	Lake beds & playa deposits
81	1924	Ross & Shannon	Challis, Idaho, U.S.A.	Lake beds & andesite flows
82	1915	Shimizu	Maze, Echigo, Japan	—
83	1924	Smirnov	Mt. Imeretin, Trans-Caucasia	Andesite
84	1941	Stewart	Loch Borolan, Scotland	Pegmatitic patch in borolanite
85	1935	Tiselius	Faeroe Island	—
85a	1926	Zeberg	Chaitsyn Cape, Arctic Russia	Augite porphyrite (clear outer portion—av. of 5 sp.)
85b	1926	Zeberg	Chaitsyn Cape, Arctic Russia	Augite porphyrite (cloudy inner portion—av. of 4 sp.) Inclusions of quartz present

microscope. Only analcite and a small amount of the unidentified phase were found, but no glass. The rest of the samples were taken out of the tubes, and then carefully dried at room temperature in a well-sealed desiccator containing phosphorus pentoxide as the drying agent, special care being taken to change the phosphorus pentoxide whenever a glassy coating of metaphosphoric acid was formed (Hillebrand, 1953). The process of weighing was continued for about a week, until the weights became constant. The samples were then heated to 900° C. and weighed.

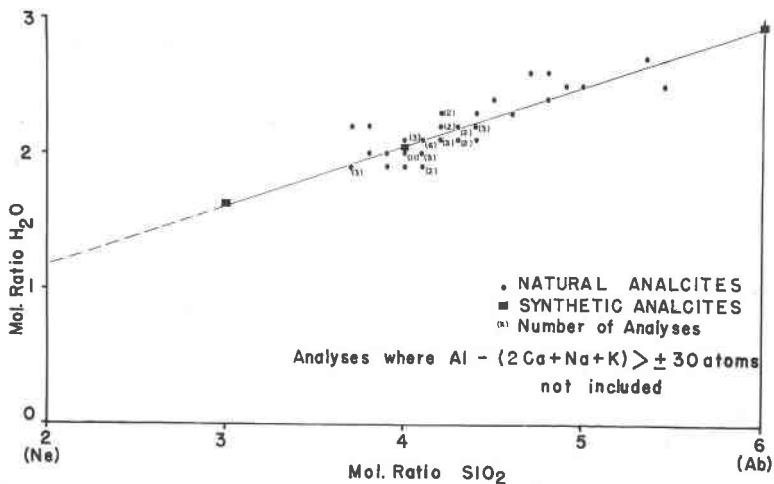


FIG. 4. The water content of synthetic and natural analcites plotted against silica.

The difference in weight was assumed to be the weight of structural water. The analyses, neglecting the small amount of the unidentified phase, are tabulated below:

Composition of glass:	$\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}$	$\text{NaAlSi}_2\text{O}_6$	$\text{NaAlSi}_3\text{O}_8$
Mol. ratio water:	1.6 ± 0.1	2.0 ± 0.1	2.9 ± 0.1

The analyses, when plotted in Fig. 4, indicated that the water content of analcite varies linearly with the variation in silica. This is in accord with the composition of natural analcites, as indicated in the figure, except the range of composition of natural analcites is more restricted.

CONCLUSION

From the present work on the composition of analcites, it becomes apparent that the analcite solid solution can be represented as follows:

$\text{NaAlSi}_{1.5}\text{O}_6, 0.75\text{H}_2\text{O}$	$\text{NaAlSi}_2\text{O}_6, \text{H}_2\text{O}$	$\text{NaAlSi}_3\text{O}_8, 1.5\text{H}_2\text{O}$
Na:Al:Si:H ₂ O	Na:Al:Si:H ₂ O	Na:Al:Si:H ₂ O
1:1:1.5:0.75	1:1:2:1	1:1:3:1.5
(natrolite composition)	(ideal analcite composition)	(albite composition)

Taylor's model indicates $48[(\text{Si}, \text{Al})\text{O}_2]$ in the unit cell. Thus there are 96 oxygen atoms and 48 Al+Si atoms in the unit cell. This number of Al+Si atoms, and consequently the number of oxygen atoms, must remain constant in order to avoid any gross distortion of the lattice—which should manifest itself in a change in space group but which has not been observed in single crystal or powder diffraction work—since the whole

framework of the lattice is built up by connecting silica and alumina tetrahedra. Thus by keeping the number of oxygen atoms constant,* we can calculate the number of other atoms and molecules in the unit cell of analcite in the following way:

Composition	O	Al	Si	Al+Si	Na	H ₂ O
NaAlSi ₅ O ₈ · 0.75H ₂ O	96	19.2	28.8	48	19.2	14.4
NaAlSi ₂ O ₆ , H ₂ O	96	16	32	48	16	16
NaAlSi ₃ O ₈ , 1.5H ₂ O	96	12	36	48	12	18

* Assuming (OH)⁻ not substituting for O⁼.

Assuming Taylor's model of analcite structure to be correct, the distribution of the 19.2 sodium atoms and 14.4 water molecules found in natrolite composition analcite is reasonable since a 24-fold position for the sodium atoms and a 16-fold position for the water molecules are available. However, it is impossible to distribute 18 H₂O molecules in albite composition analcite in a 16-fold position. An alternative suggestion, that the excess water molecules lie in some position intermediate between that of caesium in pollucite and sodium in analcite seems to be unlikely, since the albite composition analcites are fully hydrated, isotropic under the microscope, and x-ray diffraction patterns reveal a cubic symmetry. Another alternative is to assume that the excess water, i.e., the water in excess of 16 molecules, occupies some vacant sodium positions. A consideration of the radius of the water molecule, as in the case of rubidium and thallium ions (Beattie, 1954) makes it somewhat improbable, but in the absence of an alternative suggestion, this seems to be the most likely possibility since the water molecule is not as large as the rubidium or thallium ion, and only two excess water molecules have to be accommodated in the structure. It will be, perhaps, almost impossible to detect such slight distortion of the structure by x-ray methods.

ACKNOWLEDGMENT

The author is indebted to Dr. O. F. Tuttle for his constant help and guidance in carrying out this research program. Thanks are also due Drs. Rustum Roy, J. V. Smith, and Lesley Dent Glasser for their advice.

REFERENCES

- BARRER, R. M. (1950), Ion-exchange and ion-sieve processes in crystal-line zeolites: *Journ. Chem. Soc. London*, 2342-2350.
- BARRER, R. M. AND WHITE, E. A. D. (1952), Hydrothermal chemistry of silicates. Part II. Synthetic crystalline sodium aluminosilicates: *Journ. Chem. Soc. London*, 1561-1571.

- BARRER, R. M., BAYNHAM, J. W. AND MCCALLUM, N. (1953), Hydrothermal chemistry of silicates. Part V. Compounds structurally related to analcite: *Journ. Chem. Soc. London*, 4035-4041.
- BEATTIE, I. R. (1954), The structure of analcite and ion-exchanged forms of analcite: *Acta Cryst.*, **7**, 357-359.
- BRAGG, W. L. (1937), Atomic structure of minerals, Cornell University Press, Ithaca, New York, 252-255.
- COOMBS, D. S. (1955), x-ray observations on wairakite and non-cubic analcime: *Min. Mag.*, **30**, 699-708.
- DOELTER, C. (1917), Handbuch der Mineralchemie. Dresden and Leipzig, 350-357.
- GRÜNER, J. W. (1928), The use of the oscillation method in determining the structure of analcite: *Am. Mineral.*, **13**, 174-194.
- GUYER, A., INEICHEN, M. AND GUYER, P. (1957), Über die Herstellung von Künstlichen Zeolithen und ihre Eigenschaften als Molekelsiebe: *Helvetica Chimica Acta*, **40**, 1603-1611.
- HILLEBRAND, W. F., LUNDELL, G. E. F., BRIGHT, H. A. AND HOFFMAN, J. I. (1953), Applied inorganic analysis. New York, 825-826.
- NÁRAY-SZABÓ, S. v. (1938), Die Struktur des Pollucits $\text{CsAlSi}_2\text{O}_6 \cdot x\text{H}_2\text{O}$: *Zeits. Krist.*, **99**, 277-282.
- ROSS, C. S. (1928), Sedimentary analcite: *Amer. Min.*, **13**, 195-197.
- SCHIEBOLD, E. (1930), Zur Struktur von Nephelin und Analcim: *Die Naturwissenschaften*, **18**, 705-706.
- TAYLOR, W. H. (1930), The structure of analcite ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$): *Zeits. Krist.*, **74**, 1-19.
- TAYLOR, W. H. (1938), Note on the structures of analcite and pollucite: *Zeits. Krist.*, **99**, 283-290.

SELECTED REFERENCES FOR ANALCITE ANALYSES

<i>Analysis No.</i>	<i>Reference</i>
1-63	Compiled by A. HIMMELBAUER in DOELTER, C., Handbuch der Mineralchemie. 1917. Dresden and Leipzig, 350-357.
64	CURLO, G., <i>Ann. Mus. Civ. Stor. Nat. Genova</i> , 1928, 52 , 413-416. (<i>M.A.</i> , 4-376).
65	DI FRANCO, S., <i>Boll. Soc. Geol. Ital.</i> , 1926, 45 , 1-7. (<i>M.A.</i> 4-375).
66, 67	GRASSI-CRISTALDI, G. AND SCAFILE, F., <i>Annali Chim. Appl. Toma</i> , 1929, 19 , 136-140. (<i>M.A.</i> 5-83).
68	HEWETT, D. F., SHANNON, E. V., AND GONYER, F. A., <i>Proc. U. S. Nat. Mus.</i> , 1928, 73 , art. 16, 18 pp. (<i>M.A.</i> 4-324).
69	HODGE-SMITH, T., <i>Rec. Australian Museum</i> , 1929, 17 , 279-290. (<i>M.A.</i> 4-323).
70	KAŠPER, J. V., <i>Věstník Geologického Ústavu pro Čechy a Moravu</i> , 1939, 15 , 193-196 (<i>M.A.</i> 10-35).
71	KRATOCHVÍL, F., <i>Časopis Národního Musea, Praha</i> , 1933, 107 , 36-44. (<i>M.A.</i> 6-129).
72, 73, 74	LARSEN, E. S., AND BUIE, B. F., <i>Am. Mineral.</i> , 1938, 23 , 837-849. (<i>M.A.</i> 7-448).
75	LONSDALE, J. T., <i>Am. Mineral.</i> , 1928, 13 , 449-450. (<i>M.A.</i> 4-96).
76	MORGANTE, S., <i>Atti Ist. Veneto Sci. Lett. Art.</i> , 1945, 104 , 405-425. (<i>M.A.</i> 11-292).

- 77 REICHERT, R., AND ERDÉLYI, J., *Min. Petr. Mitt. (Tschermak)*, 1935, **46**, 237-255. (M.A. 6-130).
- 78 ROQUES, M., *Compt. Rend. Acad. Sci. Paris*, 1947, **225**, 946-948. (M.A. 10-294).
- 79, 80 ROSS, C. S., *Am. Mineral.*, 1928, **13**, 195-197. (M.A. 4-128).
- 81 ROSS, C. S., AND SHANNON, E. V., *Proc. U. S. Nat. Mus.*, 1924, **64**, art. 19, 1-19. (M.A. 2-301).
- 82 SHIMIZU, S., *Beitr. Min. Japan*, 1915, **5**, 295. (M.A. 1-156).
- 83 SMIRNOV, N. W., *Works Min. Inst. Moscow Univ.*, 1924, for 1923, 1-47. (M.A. 2-527).
- 84 STEWART, F. H., *Min. Mag.*, 1941, **26**, no. 172, 1-8.
- 85 TISELIUS, A., *Zeits. Physical Chem.*, 1935, *Abl. A.* **174**, 401-423. (M.A. 6-524).
- 86a and b ZEBERG, E. F., *Bull. Acad. Imp. Sci. Petrograd*, 1915, ser. 6, **9**, (part 2), 1281-1284. (M.A. 2-58).

Manuscript received July 21, 1958