Studies of the Zeolites

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Composition of Zeolites
of the Natrolite Group

and

Compositional Relations
among Thomsonites
Gonnardites, and
Natrolites

By MARGARET D. FOSTER

SHORTER CONTRIBUTIONS TO GENERAL GEOLOGY

UNITED STATES DEPARTMENT OF THE INTERIOR

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Characteristic variations in composition of natrolites, scolecites, and mesolites, indicated by published analyses

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SHORTER CONTRIBUTIONS TO GENERAL GEOLOGY

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COMPOSITION OF ZEOLITES OF THE NATROLITE GROUP

By Margaret D. Foster

ABSTRACT

A study of the analytical data on members of the natrolite group of fibrous zeolites—natrolite, scolecite, and mesolite—indicates that the scolecites are most constant in composition, with little substitution of Mg, Na, or K for Ca, and with little deviation from the theoretical value in the atomic ratios for Ca, Al, and Si or in the molecular ratios for H_2O. In many natrolites the atomic ratio for Na, or even (Na+K), is significantly less than theoretically required, and there is often not sufficient Ca present to compensate for the low Na. In some natrolites there is some evidence of replacement of Na, either by Ca or by CaAl; the CaAl also replaces an equivalent amount of Si. In others the deficiency in Na or (Na+K) cannot be accounted for in these ways. Water is generally close to the theoretical value, despite the low Na contents. There is some evidence that even small amounts of Ca tend to increase the H_2O content.

The mesolites vary widely in Ca and Na content, but three-fourths of the analyses studied are characterized by uniform and nearly theoretical Ca content and by variable Na content, which ranges from the theoretical to considerably lower than theoretical value. The nearly theoretical Ca, Al, and Si contents of these mesolites preclude either CaAl⇌NaSi or Ca⇌Na₂ types of substitution to explain the low Na contents.

The very high H_2O molecular ratios of several of the low Na natrolites and mesolites may be due to adsorbed H_2O or to hydronium ion whose presence would compensate for the low Na contents.

INTRODUCTION

Formulas for zeolites of the natrolite group—natrolite, scolecite, and mesolite—suggest minerals of fixed composition. From his study of these minerals Hey (1932, 1933, 1936) concluded that this is true with respect to the ratio Si/Al, which is quite constant, and does not deviate notably from 1.5, but that there is more variation in their content of alkalies and alkaline earths. Most natrolites contain minor amounts of K and Ca; some scolecites contain minor amounts of Na and K; and many mesolites contain more or less Ca or Na than required by the formula. He found no evidence of NaSi⇌CaAl substitution, but attributed deviation in Na or Ca content to replacement of the Na₂⇌Ca type. However, a casual inspection of the

atomic ratios of the analyses he published does not corroborate these conclusions as to replacement.

Structural studies have indicated a definite relation and close association between the cations and the water molecules. Detailed study of the natrolite structure by Meier (1960) has shown that each Na ion is surrounded by 6 oxygens (4 oxygen ions and 2 water molecules), and each H_2O molecule is close to 2 Na ions. This relation is expressed in the 1:1 ratio between Na ions and H_2O molecules. Scolecite is closely related crystallographically to natrolite and the chemical composition is similar except that the 2 Na ions and 2 H_2O molecules in natrolite are replaced by 1 Ca ion and 3 H_2O molecules in scolecite. The mesolite formula corresponds compositionally to 1 molecule of natrolite plus 2 molecules of scolecite, and the ratio of cations to water molecules is equivalent to 1:1 for the Na cations plus 1:3 for the Ca ions. Because of the close structural association between the cations and the water molecules, it would be expected that replacement of one cation by another or deficiency in cationic content would be reflected in H_2O content.

It seemed desirable, therefore, to reexamine analyses of these zeolites to learn the kind and extent of variation in composition, and the relation between variation in composition and H_2O content.

The analyses used in this study were carefully selected from the literature, particularly with respect to age, summation of constituents, and summation of the atomic ratios of the tetrahedral constituents. Analyses included in the study were restricted to those made since 1900, except where especially noted, for which the sum of the constituents was not less than 99.70, or more than 100.50, and for which the atomic ratios for Si and Al totaled 10±0.10. For purposes of comparsion all the atomic ratios for the analyses were calculated on the basis of 20 oxygen atoms. According to Hey's (1955) formulas, calculations so based give quarter-cell atomic ratios for natrolite and scolecite, and twelfth cell ratios for mesolite.

NATROLITE

$Na_{4.0}Al_{4.0}Si_{6.0}O_{20}\cdot 4.0\ H_2O$

The 27 analyses used to study the composition of natrolite are given in table 1, with their atomic ratios. The Na_2O content of these analyses ranges from a high of 16.73 percent to a low of 14.43 percent, or, in terms of atomic ratios, from $Na_{4.11}$ to $Na_{3.57}$. K_2O, reported in about two-thirds of these analyses, ranges from 0.01 to 0.59 percent (0.10 K atomic ratio) except in No. 26,

which contains 1.27 percent K_2O (0.20 K atomic ratio). In most of the analyses the atomic ratio for Na is less than the theoretical 4.00 indicated in the formula above. Even with K, the sum of the univalent cations (Na+K) is less than 4.00 in about three-fourths of the analyses, and is 3.85 or less in about one-half of them. In several analyses (Na+K) is less than 3.70.

CaO is reported in all but six of the analyses, but the amounts reported are generally low. Only six analyses reported more than 0.75 percent CaO (about

TABLE 1.—*Analyses of natrolite and their calculated atomic ratios*

[In order of decreasing Na₂O content]

No.	Composition (percent)							Atomic ratio					H₂O			Positive charge
	SiO₂	Al₂O₃	CaO	Na₂O	K₂O	H₂O	Total	Si	Al	Ca	Na	K	Determined	Calculated	Difference	
1	46.93	27.02	--------	16.73	--------	9.58	100.26	5.95	4.03	--------	4.11	--------	4.05	4.11	−0.06	4.11
2	47.09	26.99	--------	16.46	0.01	9.80	100.35	5.97	4.03	--------	4.04	0.00	4.14	4.04	+.10	4.04
3	47.1	27.1	--------	16.4	--------	9.44	100.04	5.96	4.04	--------	4.02	--------	3.99	4.02	−.03	4.02
4	47.40	26.88	0.05	16.25	.11	9.67	100.36	6.00	4.01	0.00	3.98	.02	4.08	4.02	+.06	4.00
5	46.95	27.06	.27	15.97	--------	9.58	99.83	5.96	4.05	.04	3.93	--------	4.06	4.05	+.01	4.01
6	46.72	26.51	.24	15.95	.52	[1]9.08	[2]99.91	5.97	3.99	[2].05	3.95	.08	3.79	4.18	−.40	4.13
7	47.32	26.30	.50	15.95	--------	9.50	99.57	6.02	3.94	.07	3.94	--------	4.04	4.15	−.11	4.08
8	47.17	26.84	.12	15.89	.02	[3]9.58	99.74	6.00	4.02	.02	3.92	--------	4.06	3.98	+.08	3.96
9	47.22	27.21	--------	15.86	.06	9.70	100.05	5.98	4.06	--------	3.90	--------	4.10	3.90	+.20	3.90
10	47.80	26.81	--------	15.83	--------	9.69	100.13	6.04	3.99	--------	3.88	--------	4.08	3.88	+.20	3.88
11	47.69	27.14	--------	15.74	--------	[4]9.56	100.13	6.02	4.03	--------	3.85	--------	4.02	3.85	+.17	3.85
12	46.91	27.10	.63	15.65	.14	9.72	100.15	5.95	4.05	.08	3.85	.02	3.97	4.11	−.14	4.03
13	46.38	27.36	.83	15.63	.13	9.28	99.61	5.90	4.10	.11	3.85	.02	3.94	4.20	−.26	4.09
14	47.33	27.13	.10	15.63	--------	[5]9.67	99.86	6.00	4.05	.01	3.84	--------	4.03	3.87	+.16	3.86
15	46.53	26.63	.44	15.53	.44	9.62	[6]100.65	5.96	.4.02	[5].08	3.85	[5].07	4.12	4.16	−.04	4.08
16	47.45	27.40	.07	15.45	.42	9.16	[7]100.20	5.98	4.07	.01	3.77	.07	3.86	3.87	−.01	3.86
17	47.34	27.17	.48	15.42	.28	9.47	[8]100.17	5.98	4.04	.06	3.77	.04	3.99	3.99	.00	3.93
18	47.60	27.40	.13	15.36	.23	9.47	100.19	6.00	4.06	.02	3.74	.04	3.98	3.84	+.14	3.82
19	47.15	27.39	.30	15.27	.50	9.53	100.14	5.96	4.08	.04	3.74	.08	4.02	3.94	+.08	3.90
20	47.38	27.63	.54	14.96	.41	9.58	100.50	5.96	4.10	.07	3.65	.06	4.02	3.92	+.10	3.85
21	46.60	27.21	Trace	14.80	.31	10.24	[9]99.94	5.98	4.12	--------	3.68	.05	4.38	3.73	+.65	3.73
22	47.33	27.67	.22	14.74	.50	9.64	100.10	5.98	4.12	.03	3.60	.08	4.06	3.77	+.29	3.74
23	46.6	27.2	1.3	14.7	<.01	9.6	99.4	5.94	4.09	.18	3.63	--------	4.04	4.17	−.13	3.99
24	47.29	27.56	.80	14.63	.59	9.40	100.27	5.96	4.09	.11	3.57	.10	3.95	4.00	−.05	3.89
25	44.85	27.94	2.00	14.47	--------	[10]10.68	[11]100.14	5.78	4.24	.28	3.62	--------	4.37	4.46	−.09	4.18
26	47.22	26.94	1.05	14.45	1.27	9.28	100.21	5.98	4.02	.14	3.54	.20	3.92	4.16	−.24	4.02
27	46.42	27.27	1.04	14.43	.47	9.64	[12]99.86	5.94	4.11	.14	3.57	.08	4.11	4.07	+.04	3.93

[1] Includes 0.20 H₂O−.
[2] Includes 0.20 Fe₂O₃, 0.12 MgO (0.02 Mg atomic ratio), 0.08 P₂O₅, and 0.49 insoluble.
[3] Includes 0.07 Fe₂O₃ and 0.05 MgO.
[4] Includes 0.34 H₂O−.
[5] Includes 0.13 H₂O−.
[6] Includes 1.34 Fe₂O₃ and 0.12 MgO (0.02 atomic ratio).

[7] Includes 0.25 Fe₂O₃.
[8] Includes 0.01 Fe₂O₃.
[9] Includes 0.52 Fe₂O₃, 0.06 FeO, 0.05 MgO, and 0.15 TiO₂.
[10] Includes 0.51 H₂O−.
[11] Includes 0.20 Fe₂O₃-FeO.
[12] Includes 0.59 Fe₂O₃.

LOCALITY AND REFERENCE FOR ANALYSIS IN TABLE 1

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0.10 Ca atomic ratio), and only one reported as much as 2.00 percent CaO (0.28 Ca atomic ratio). Several of the higher CaO values were reported in analyses significantly deficient in Na_2O, and thus raised the cationic content. However, little or no CaO was reported in several analyses that were significantly deficient in $Na_2O(+K_2O)$.

The Si and Al atomic ratios are generally 6.00 ± 0.10 and 4.00 ± 0.10, respectively. Only one analysis, No. 25, yields a Si atomic ratio with a greater deviation, —0.22. Deviations in Al content greater than 0.10 are slightly more common, being found in four analyses. The greatest deviation, +0.24 is in analysis No. 25.

The atomic ratios for Si, Al, Na, and Ca in No. 25 indicate a slight CaAl replacement of NaSi. This type of replacement is also indicated in No. 13. Ca replacement of $Na_2(+K_2)$ is indicated in No. 23, and No. 26. A little of both types may be suggested by the atomic ratios of Nos. 12 and 27. In most of the analyses, however, the atomic ratios for Ca are so low, and the Si and Al ratios are so close to the theoretical values that the low Na ratios cannot be explained by either type of replacement.

The H_2O content of these natrolites is very constant and very close (±0.15) to the theoretical 4.00 in 24 of the 27 analyses, even though (Na+K) is more than 0.20 deficient in one-third of the analyses. For some of the analyses that are low in Na but for which the atomic ratio of H_2O is near 4.00 or even higher, the H_2O value can be accounted for if the Ca present is considered as contributing to the H_2O content in the 3:1 ratio as in scolecite. In No. 27, for example, the atomic ratio for (Na+K) is only 3.65, and consequently, accounts for a H_2O molecular ratio of only 3.65 H_2O. However, the atomic ratio of Ca, 0.14, tripled (0.42) and added to 3.65 gives a calculated H_2O ratio of 4.07, compared to the determined value of 4.11. Other analyses in which the atomic ratio for (Na+K) is much lower than the H_2O molecular ratio and for which it is necessary to include the Ca value tripled to obtain a calculated H_2O value comparable to the determined value are Nos. 17, 20, 24, and 25. This suggests that Ca is an intrinsic constituent of these natrolites. In other analyses, as in No. 26, inclusion of the Ca tripled in the calculated water computation yields a H_2O value that is somewhat higher than the determined value, suggesting that some, at least, of the Ca may be extraneous to the natrolite molecule. In other analyses, as in No. 21, the determined water is considerably higher than the calculated. This analysis reports no Ca. Such a high H_2O content may be due to adsorption of H_2O in a humid atmosphere by the finely ground sample before analysis, H_2O- being seldom reported in analyses of zeolites, or a high H_2O content may be

due to the presence of hydronium ions, which would compensate for the low Na content.

SCOLECITE

$$Ca_{2.0}Al_{4.0}Si_{6.0}O_{20}\cdot6.0\ H_2O$$

The 16 analyses used to study the composition and water content of scolecite are given in table 2, together with their atomic ratios calculated on the basis of 20 oxygen atoms. The CaO content of these analyses is quite constant, ranging only between 13.58 and 14.86 percent. The corresponding atomic ratio for Ca ranges only between 1.89 and 2.09, or 2.0 ± 0.11. MgO is reported in only four of the analyses. The highest amount is only 0.32 percent or an atomic ratio for Mg of only 0.06. Na_2O was reported in one-half of the analyses, most of which also reported K_2O. However, the amounts found were low, and the highest atomic ratio for (Na+K) in any of the analyses was only 0.20.

For most of the analyses the atomic ratios for Si and Al were within 0.10 of the theoretical 6.00 and 4.00, respectively. As these values and those for Ca are so close to the theoretical, there is little indication of replacement except in analyses 14, 15, and 16, in which the atomic ratios for Ca are the lowest and those for (Na+K) the highest. In No. 15 the atomic ratio for (Na+K), 0.20, and the deficiency in the atomic ratios for Ca, 0.08, suggest slight replacement of Ca by $(Na+K)_2$. The deviation in the atomic values of No. 15 for Si and Al of —0.12 and +0.14, respectively, would suggest CaAl replacement for NaSi if the Ca were not already lower and the Na higher than the theoretical values. In Nos. 14 and 16 replacement is of the $Na_2\longrightarrow Ca$ type.

The molecular ratios for H_2O for all the analyses are within 0.20 of the theoretical value except for No. 2, for which H_2O is low, 5.71, and No. 6, for which H_2O is high, 6.32. However, the high H_2O molecular value in No. 6 can be partially accounted for if H_2O equivalent to Na is added to the tripled Ca value. Molecular values of H_2O, calculated on the basis of a 1:3 relation between Ca atoms and H_2O molecules and 1:1 relation between Na atoms and H_2O molecules, agree fairly well with the determined H_2O molecular ratios. For analyses 15 and 16, as well as for No. 6, it is necessary to include H_2O equivalent to the (Na+K) present to produce a calculated H_2O value more nearly approximating the determined H_2O value.

MESOLITE

$$Na_{1.33}Ca_{1.33}Al_{4.0}Si_{6.0}O_{20}\cdot5.33\ H_2O$$

Analyses of 17 mesolites, together with their atomic ratios calculated on the basis of 20 oxygen atoms, are given in table 3. For 13 of the 17 analyses, Nos. 4–16, the atomic ratio for Ca is close to the theoretical value

TABLE 2.—*Analyses of scolecite and their calculated atomic ratios*

[In order of decreasing CaO content]

No.	Composition (percent)								Atomic ratio						H_2O		
	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	H_2O	Total	Si	Al	Ca	Mg	Na	K	De-termined	Cal-culated	Differ-ence
1	45.16	25.90	14.86	-------	0.16	0.06	13.66	99.80	5.94	4.01	2.09	-------	0.04	0.00	5.99	6.31	−0.32
2	45.22	27.25	14.67	0.08	Trace	None	13.20	100.42	5.86	4.16	2.04	0.00	.00	.00	5.71	6.12	−.41
3	45.9	26.26	14.63	-------	-------	-------	13.77	100.56	5.97	4.02	2.04	-------	-------	-------	5.97	6.12	−.15
4	45.00	26.77	14.50	-------	-------	-------	13.67	99.94	5.89	4.13	2.03	-------	-------	-------	5.97	6.09	−.12
5	47.08	25.16	14.59	-------	-------	-------	[1] 13.40	100.23	6.11	3.84	2.02	-------	-------	-------	5.80	6.06	−.26
6	45.56	25.70	14.23	-------	.50	.11	14.43	100.53	5.98	3.98	2.00	-------	.13	.02	6.32	6.15	+.17
7	46.10	26.32	14.22	-------	.12	-------	13.60	100.36	5.98	4.02	1.98	-------	.03	-------	5.89	5.97	−.08
8	46.10	25.05	14.17	.32	-------	.03	[2] 13.91	[3] 100.13	6.06	3.88	1.99	.06	-------	.00	6.05	6.15	−.10
9	45.59	26.25	14.10	.19	.33	.04	13.99	100.49	5.95	4.04	1.97	.04	.09	.00	6.09	6.12	−.03
10	46.40	26.69	14.10	-------	-------	-------	13.53	100.72	5.98	4.06	1.95	-------	-------	-------	5.82	5.85	−.03
11	45.71	26.87	14.08	-------	-------	-------	13.88	100.54	5.94	4.11	1.96	-------	-------	-------	6.01	5.98	+.03
12	46.17	25.83	13.96	.12	-------	-------	13.88	99.96	6.03	3.97	1.95	.02	-------	-------	6.05	5.91	+.14
13	45.96	26.10	13.91	-------	-------	-------	13.97	99.94	6.10	4.02	1.95	-------	-------	-------	6.10	5.85	+.25
14	45.78	26.23	13.66	-------	.70	.11	13.44	[4] 99.99	5.97	4.03	1.91	-------	.18	.02	5.85	5.93	−.08
15	44.63	26.68	13.63	-------	.66	.18	13.50	99.28	5.88	4.14	1.92	-------	.17	.03	5.94	5.96	−.02
16	46.37	25.80	13.58	-------	.64	.13	13.84	100.36	6.04	3.96	1.89	-------	.16	.02	6.02	5.85	−.17

[1] Ignition loss.
[2] Includes 0.13 H_2O-.
[3] Includes 0.55 Fe_2O_3.
[4] Includes 0.07 Fe_2O_3.

LOCALITY AND REFERENCE FOR ANALYSES IN TABLE 2

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of 1.33, being 1.33±0.07. In the other four, Ca is about 0.20 higher than theoretical value in three, (Nos. 1, 2, and 3), and 0.12 lower in one, (No. 17). In the three analyses in which Ca is high, Na is low; in No. 17, in which Ca is low, Na is high. In this last analysis the relation between Ca and Na can be interpreted as replacement of 0.12 Ca by 0.22 Na, but the relations between Ca and Na and between Si and Al in Nos. 1, 2, and 3, do not permit such an interpretation. In the group of 13 in which Ca is very constant and close to the theoretical value, the amount of Na present varies considerably, and in most is deficient. However, because of the fact that several contain a little K, or that Ca is slightly greater than the theoretical 1.33, the cationic charge is 4.00±0.10 for more than half of these analyses. In the analyses for which the positive charge is less than 3.90, slight adjustments in the amounts of Si and Al present produce the lower negative charges that just balance the lower positive charges.

The Si ratio is 6.00±0.10 for all the analyses given in table 3, and the Al ratio is 4.00±0.10 for all but two, Nos. 10 and 14, in which it is 4.11 and 4.16, respectively. However, as the respective Si ratios for these analyses are not low by similar amounts, replacement of the CaAl—→NaSi type is not indicated. Nor is similar

replacement, or the reverse, except in a very slight degree, perhaps, indicated in any of the other analyses because of the close agreement of the Si and Al ratios with the theoretical value.

For most of the analyses the determined H_2O values yield molecular ratios that agree fairly well with the theoretical values. Furthermore, molecular H_2O ratios calculated on the basis of a 1:1 relation between Na(+K) ions and H_2O molecules, and a 1:3 relation between Ca ions and H_2O molecules, agree within 0.20 molecule with the H_2O ratios based on the determined H_2O, except for analyses Nos. 9, 14, and 16. For Nos. 9 and 14, the determined H_2O ratios are very high, 5.77 and 5.85, respectively. For No. 16 the determined H_2O ratio is only 5.42, quite close to the theoretical 5.33, but it is much higher than the calculated H_2O because of the low Ca and Na content of this sample. Na is also low in Nos. 9 and 14. The high H_2O content reported for these analyses may be due to hydronium ion, whose presence would compensate for their low Na content. On the other hand, these high H_2O values may be due to adsorption of H_2O before analysis by the finely ground specimen in a humid environment. In most of these analyses only total water was reported: H_2O- and H_2O+ were differentiated only in analysis

TABLE 3.—*Analyses of mesolite, and their calculated atomic ratios*

[In order of decreasing CaO content]

No.	Composition (percent)							Atomic ratio								Charge	
													H₂O				
	SiO₂	Al₂O₃	CaO	Na₂O	K₂O	H₂O	Total	Si	Al	Ca	Na	K	Deter-mined	Calcu-lated	Differ-ence	Positive	Negative
1	44.96	26.30	11.15	4.10	--------	13.20	99.71	5.90	4.07	1.57	1.04	--------	5.78	5.75	+0.03	4.18	4.19
2	44.40	25.63	10.97	5.02	--------	13.93	99.95	5.90	4.01	1.56	1.29	--------	6.17	5.97	+.20	4.41	4.37
3	45.66	26.11	10.90	4.46	--------	(¹)	100.66	5.95	4.01	1.52	1.13	--------	¹5.88	5.69	+.19	4.17	4.17
4	45.97	27.00	10.10	4.98	--------	12.78	100.83	5.92	4.10	1.39	1.24	--------	5.49	5.41	+.08	4.02	4.02
5	47.13	26.02	10.09	4.50	0.11	12.17	100.02	6.06	3.94	1.39	1.12	0.02	5.22	5.31	−.09	3.92	3.94
6	46.98	26.43	10.06	4.57	.05	11.94	100.03	6.03	3.99	1.38	1.13	--------	5.11	5.27	−.16	3.89	3.91
7	46.05	26.84	10.00	3.82	.79	12.30	99.80	5.96	4.09	1.39	.96	.13	5.31	5.26	+.05	3.87	3.89
8	46.01	26.66	9.88	4.66	.20	12.69	²100.48	5.97	4.07	1.37	1.17	.03	5.49	5.31	+.18	3.94	3.91
9	46.08	26.64	9.86	4.20	--------	13.30	100.08	5.99	4.08	1.37	1.05	--------	5.77	5.16	+.61	3.79	3.80
10	46.15	27.04	9.73	4.64	.06	12.36	99.98	5.96	4.11	1.34	1.16	--------	5.32	5.18	+.14	3.84	3.83
11	46.50	26.58	9.72	4.97	--------	12.29	100.06	5.99	4.04	1.34	1.24	--------	5.28	5.26	+.02	3.92	3.92
12	46.04	26.32	9.72	5.32	.40	12.48	100.28	5.96	4.02	1.35	1.34	.06	5.39	5.45	−.06	4.10	4.10
13	45.97	25.98	9.69	4.79	--------	³13.38	99.81	6.01	4.00	1.36	1.22	--------	5.25	5.30	−.05	3.94	3.96
14	45.70	27.16	9.67	4.24	--------	(⁴)	100.13	5.94	4.16	1.35	1.07	--------	⁴5.85	5.12	+.73	3.77	3.76
15	46.71	26.45	9.35	5.33	.11	12.56	100.51	6.01	4.01	1.29	1.33	.01	5.39	5.21	+.18	3.92	3.93
16	46.44	26.86	8.84	4.60	.32	12.67	⁵99.93	6.00	4.09	⁵1.26	1.15	.05	5.42	4.98	+.44	3.72	3.73
17	46.17	26.88	8.77	6.19	--------	12.16	100.17	5.95	4.08	1.21	1.55	--------	5.23	5.16	+.07	3.97	3.96

¹ Ignition loss, 13.53.
² Includes 0.38 Fe₂O₃ (Fe³⁺ atomic ratio=0.04).
³ Includes 1.34 H₂O−.

⁴ Ignition loss, 13.36.
⁵ Includes 0.20 MgO (Mg atomic ratio=0.04).

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13. If the value for total water had been used to calculate the determined H₂O molecular ratio for No. 13, the H₂O ratio would have been 5.84, instead of 5.25, the value obtained when the H₂O+ value was used in the calculation. Thus H₂O ratios based on total H₂O values may be high because of adsorbed water.

TABLE 4.—*Analyses of high-Na mesolites*

PERCENT

	SiO₂	Al₂O₃	CaO	NaO	K₂O	H₂O	Total
1	40.03	27.88	6.03	10.05	0.40	¹11.10	²100.29
2	41.15	29.49	5.33	11.02	.25	13.52	100.76
3	40.59	29.69	5.06	11.00	.51	13.58	100.43

ATOMS PER TWELFTH CELL

	Si	Al	Ca(+Mg)	Na(+K)	H₂O
1	5.48	4.50	0.92	2.73	5.07
2	5.45	4.60	.76	2.86	5.97
3	5.41	4.66	.72	2.92	6.03

¹ Includes 3.12 H₂O−.
² Includes 0.85 Fe₂O₃, 0.59 FeO, 0.22 MgO (0.04 atomic ratio), and 0.02 TiO₂.

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Three analyses of high Na mesolite are shown in table 4. These analyses are very similar to each other but very different from the mesolite analyses given in table 3, being respectivley lower in Si and Ca, and higher in Al and Na. Such compositions as indicated by these analyses cannot be derived from theoretical mesolite by either NaSi⇌CaAl or Na₂⇌Ca replacement. They can only be derived from mesolite by replacement of an average of about 0.55 CaSi by 0.55 Na₃Si. These analyses are very similar to some of the analyses of gonnardite published by Meixner, Hey, and Moss (1956) and by Kostov (1958), and to some high-Na thomsonites published or cited by Hey (1932). Such compositions can be derived from thomsonite by a combination of Na₂—→Ca and NaSi—→CaAl replacement.

DISCUSSION

The most significant finding resulting from this study of analyses of the natrolite group of zeolites is that the amounts of Si, Al, and Ca present usually agree very well with the amounts required by the formulas but that the amount of Na present is often deficient. As a consequence, scolecites are the most uniform in com-
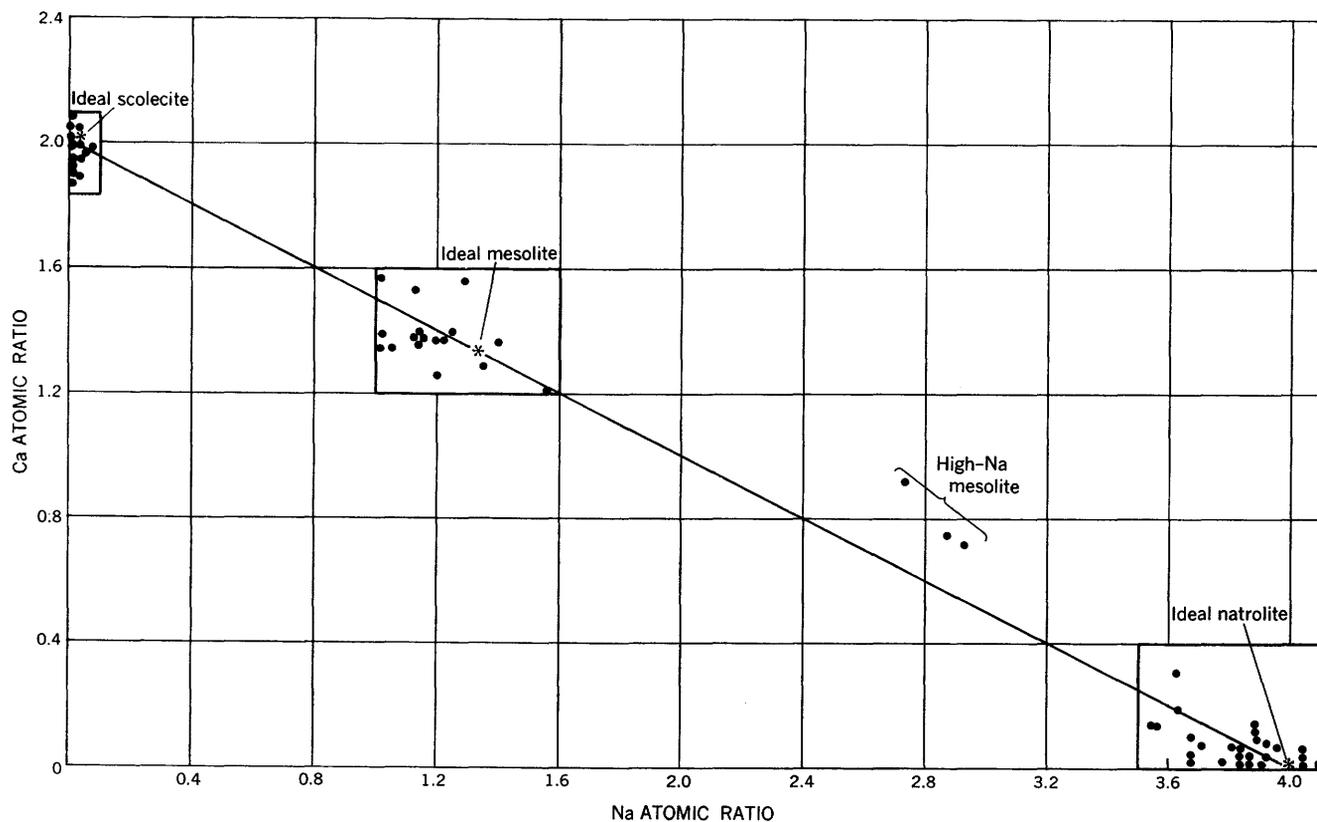
FIGURE 1.—Relation between $Ca(+Mg)$ and $Na(+K)$ in natrolites, scolecites, and mesolites.

position and conform most closely with the requirements of the formula, and natrolites deviate most from the requirements of the formula. In mesolites the Ca is usually close to the theoretical value, but the Na is often significantly lower than the theoretical value. As the other constituents deviate so little from the theoretical, the deficiency in Na cannot be interpreted, generally, in terms of either type of replacement, $Ca\rightarrow Na_2$ or $CaAl\rightarrow NaSi$. In some natrolites there is sufficient Ca or K present to produce a positive cationic charge close to the theoretical 4.00. In some mesolites also the Ca, although close to the theoretical, is enough higher to bring the positive charge close to 4.00. However, in other natrolites and mesolites the positive cationic charge is only 3.75, or even less. Slight adjustments in the amounts of Si and Al present produce the lower negative charges that just balance the lower positive charges.

The relation between Ca and Na in these zeolites is shown graphically in figure 1. The points representing the relation between Ca and Na in scolecites all fall in a very small area closely grouped around the point representing ideal scolecite, whereas the points representing the relation between Ca and Na in mesolites and natrolites are more scattered. Most of the points representing the relation between Ca and Na in analyses

of mesolites and natrolites fall left of the points representing ideal mesolite and ideal natrolite, respectively, thus indicating lower Na than ideally presumed to be present. However, three points representing the relation between Ca and Na in samples of high Na mesolite fall lower and far to the right of the mesolite area; closer to the natrolite area than to the mesolite area. In composition these analyses resemble gonnardites or high-Na thomsonites rather than mesolites.

Most H_2O molecular ratios based on reported H_2O contents are close to the theoretical value specified in the formula. Also, most of the H_2O values calculated from the $Ca(+Mg)$ and $Na(+K)$ present agree within 0.20 molecule of the H_2O values based on the amount of H_2O reported in the analysis. In general the determined H_2O ratios are higher than the calculated ratios. A few determined H_2O values are very high. As most zeolite analyses report only total H_2O, and do not differentiate H_2O- and H_2O+, these higher values for determined H_2O may be due to adsorbed H_2O, which is probably very slight in most of the samples analyzed but in some may be considerable, and so produce an unrealistically high H_2O content particularly if the finely powdered sample has been in a humid environment before analysis. The dehydration curves of Koizumi (1953) and Peng (1955) indicate that H_2O

that is an intrinsic part of the structure does not begin to come off below about 150° C; consequently determination of H_2O- at 110° C is perfectly feasible. It is therefore recommended that H_2O- be routinely determined in the zeolites.

The highest H_2O values in both the natrolites and the mesolites occur in analysis that are very low in Na and that have the lowest positive charges. It may be, therefore, that these high H_2O values are caused by hydronium ions which compensate for the low cationic content of the zeolite.

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Studies of the Zeolites

Compositional
Relations among
Thomsonites
Gonnardites
and Natrolites

By MARGARET D. FOSTER

SHORTER CONTRIBUTIONS TO GENERAL GEOLOGY

GEOLOGICAL SURVEY PROFESSIONAL PAPER 504-E

Relations among thomsonites, high-sodium thomsonites, gonnardites, high-sodium mesolites, and natrolites as indicated by published analyses
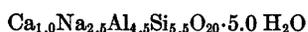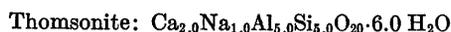
SHORTER CONTRIBUTIONS TO GENERAL GEOLOGY

Studies of the Zeolites

COMPOSITIONAL RELATIONS AMONG THOMSONITES, GONNARDITES, AND NATROLITES
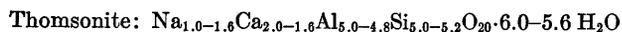
By Margaret D. Foster

ABSTRACT

A study of post-1885 analyses of thomsonite selected from Hey's 1932 compilation confirms the isomorphous series between thomsonite and faroelite. This isomorphous series, which is characterized by replacement of CaAl by NaSi, was recognized by Winchell (1925, 1926) and Hey (1932). Hey's formula for gonnardite is related to thomsonite in the same way and carries this line of replacement a step beyond faroelite. However, the total number of cations, and the relation between Si and Al and Ca and Na in analyses of gonnardite, including those published by Meixner, Hey, and Moss (1956) indicate replacement of Ca by Na_2 as well as replacement of Ca as CaAl by NaSi. Similar numbers of total cations, and similar relations between Si and Al and Ca and Na were also found in some analyses of high Na thomsonites and in high Na mesolites. Plotted points representing the relation between Ca and Na in these analyses fall, not along the thomsonite-faroelite line, but along a line representing dual replacement, to the same degree, of Ca by Na_2 and of CaAl by NaSi. Such dual replacement of Ca in thomsonite leads theoretically to natrolite:

Thomsonite: $Ca_{2.0}Na_{1.0}Al_{5.0}Si_{5.0}O_{20} \cdot 6.0\ H_2O$

$Ca_{1.0}Na_{2.5}Al_{4.5}Si_{5.5}O_{20} \cdot 5.0\ H_2O$

Natrolite: $Ca_{.0}Na_{4.0}Al_{4.0}Si_{6.0}O_{20} \cdot 4.0\ H_2O$

The analyses alone suggest an isomorphous series between thomsonite and natrolite, with gonnardite as the intermediate member.

For such a series only formulas indicating ranges of composition are adequate. As there appears to be no natural hiatus in composition between thomsonite and gonnardite, the division was arbitrarily fixed at the point where Ca and Na are equal. The suggested range formulas for the series are:

Thomsonite: $Na_{1.0-1.6}Ca_{2.0-1.6}Al_{5.0-4.8}Si_{5.0-5.2}O_{20} \cdot 6.0-5.6\ H_2O$

Gonnardite: $Na_{1.6-3.4}Ca_{1.6-0.4}Al_{4.8-4.2}Si_{5.2-5.8}O_{20} \cdot 5.6-4.4\ H_2O$

Natrolite: $Na_{3.4-4.0}Ca_{0.4-0.0}Al_{4.2-4.0}Si_{5.8-6.0}O_{20} \cdot 4.4-4.0\ H_2O$

Although thomsonite and natrolite have similar aluminosilicate frameworks, they differ considerably in detail. Thus there may be a structural hiatus between thomsonite and natrolite like that between muscovite and lepidolite. No study has been made of the structure of gonnardite. The indices of refraction of gonnardite are intermediate between those of thomsonite and natrolite, those of thomsonite the higher, and those of natrolite the lower. However, the optic sign of gonnardite is negative, and those of thomsonite and of natrolite are positive.

INTRODUCTION

The formulas for thomsonite and gonnardite, like those for natrolite, mesolite, and scolecite, suggest minerals of fixed and definite composition, although they are well known to be quite variable in composition. Winchell (1925) recognized that there is isomorphous $NaSi \rightleftharpoons CaAl$ replacement in thomsonite, as between thomsonite, $Ca_{2.0}Na_{1.0}Al_{5.0}Si_{5.0}O_{20} \cdot 6.0\ H_2O$ and $Ca_{1.25}Na_{1.75}Al_{4.25}Si_{5.75}O_{20} \cdot 5.0\ H_2O$. Hey (1932) concurred with this view but considered that there is also considerable $Na_2 \rightleftharpoons Ca$ replacement, which Winchell had considered unimportant. However Hey's formula for gonnardite, $2[Na_2CaAl_4Si_6O_{20} \cdot 7H_2O]$, is related to thomsonite by $NaSi \rightarrow CaAl$ replacement only, although atomic ratios derived from analyses of gonnardite, including those published by Meixner, Hey, and Moss (1956), indicate both $NaSi \rightarrow CaAl$ and $Na_2 \rightarrow Ca$ substitution.

The relation between H_2O and the cations in thomsonite is less simple than in natrolite or mesolite. Taylor, Meek, and Jackson (1933) assume the environment of the Na ion and one of the Ca ions to be similar to that of the Na in natrolite, except for an additional H_2O molecule that increases the coordination from sixfold to sevenfold with 4 oxygen ions and 3 water molecules. The other Ca ion they assume to be in eightfold coordination, with 6 oxygen ions and 2 water molecules. The relation between water molecules and cations is as though there were 1 water molecule for each Na ion, 2 for one-half of the Ca ions and 3 for the other half, or an average of 2.5 to 1 for all the Ca ions.
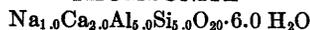
The water content of gonnardite seems to be in doubt. Hey (1955) gives the formula as $2[Na_2CaAl_4Si_6O_{20} \cdot 7H_2O]$, but in 1956 Meixner, Hey, and Moss give the formula as $[(Ca,Na)_{6-8}(Si,Al)_{20}O_{40} \cdot 12\ H_2O]$, and Deer, Howie, and Zussman (1963 p. 359) give the formula as $Na_2Ca[(Al,Si)_5O_{10}]_2 \cdot 6\ H_2O$. These amounts of water seem high in a fibrous zeolite in which Na is the principal cation. In other fibrous zeolites in which Na is a

principal cation—natrolite and mesolite—the ratio of H_2O molecules to Na ions is 1:1, compared to the ratio of 3:1 or 2.5:1 for Ca-dominant zeolites like scolecite and thomsonite. As Na is the predominant cation in gonnardite, H_2O would be expected to be lower in gonnardite than in thomsonite, rather than the same or higher as indicated by these formulas. It is significant that in the analyses of gonnardite given by Meixner, Hey, and Moss, the two having the highest Na content yield molecular ratios for H_2O of only 5.14 and 5.19.

The purpose of this investigation is to study the degree and kind of variation in composition that occurs in the thomsonites and gonnardites, and the relation of these minerals to each other, and to examine the problem of the water content of gonnardite. The analyses of thomsonite used were selected from those reported or cited by Hey (1932), using only analyses published after 1885, in which the sum of the tetrahedral atoms was 10.0 ± 0.10. In addition to the analyses of gonnardite published by Meixner, Hey, and Moss, several other recent analyses from the literature were also used.

Atomic ratios were calculated from the analyses on the basis of 20 oxygen atoms, and represent, according to Hey's (1955, p. 166) formulas, quarter-cell values for thomsonites and half-cell values for gonnardites.

THOMSONITE
$$Na_{1.0}Ca_{2.0}Al_{5.0}Si_{5.0}O_{20}\cdot 6.0\ H_2O$$

Atomic ratios for selected post-1885 analyses of thomsonite reported or cited by Hey (1932) are given in tables 1 and 2 together with calculated values for H_2O. The atomic ratios show wide ranges in the values for Si and Al. The ranges for Ca and Na are even greater, from 2.14 to 1.00 for Ca, from 0.74 to 2.71 for Na, and from 2.58 to 3.71 for (Ca+Na). However, Ca values greater than 2.00 are found in only four analyses and these values are 2.02, 2.04, 2.07, 2.14. Values for Na less than 1.00, were found in only seven; of these seven, only three, 0.89, 0.88, and 0.74, are less than 0.90. Both types of replacement recognized in thomsonite affect the Ca and Na content, consequently the kind and amount of replacement can be estimated only by other deviations in composition. A Si value greater than 5.00, the theoretical amount according to the above formula for thomsonite, together with an Al value deficient by about the same amount, indicates replacement of an equivalent amount of Ca by Na. A positive difference in the expression [(Ca+Na)−3.00] indicates that this amount of Ca has been replaced by Na_2; a negative result indicates the amount of Ca replacing Na_2. The fact that in the ranges in Ca and Na quoted above most Ca values are less than 2.0, with few significantly above, and that most Na values are greater than 1.00, with few significantly less, indicates that replace-

TABLE 1.—*Atomic ratios calculated from analyses of thomsonite reported by Hey, 1932*

[Numbers refer to Hey, 1932, table 1, p. 54-55]

| No. | Ca(+Mg) | Na(+K) | (Ca+Na) | Al | Si | H₂O | | |
						Determined	Calculated	Difference
1	1.62	1.48	3.10	4.52	5.43	6.34	5.53	+0.81
2	1.67	1.20	2.87	4.57	5.42	5.58	5.38	+.20
3	1.84	.74	2.58	4.58	5.46	6.10	5.34	+.76
4	1.71	.89	2.60	4.62	5.46	6.44	5.17	+1.27
5	1.00	2.71	3.71	4.62	5.36	5.48	5.21	+.27
6	1.41	1.70	3.11	4.62	5.40	6.44	5.22	+1.22
7	1.72	1.18	2.90	4.65	5.36	5.50	5.48	+.02
8	1.76	1.24	3.00	4.68	5.29	6.12	5.64	+.48
9	1.45	1.71	3.16	4.70	5.32	5.46	5.33	+.13
10	1.82	1.24	3.06	4.73	5.23	5.92	5.79	+.13
11	1.74	1.26	3.00	4.78	5.23	5.89	5.61	+.28
12	1.98	1.22	3.20	4.87	5.06	5.82	6.17	−.35
13	2.08	.88	2.96	4.90	5.06	6.10	6.08	+.02
14	1.98	.97	2.95	4.93	5.07	5.61	5.92	−.31
15	2.00	1.04	3.04	5.03	4.97	5.95	6.04	−.09
16	2.02	.94	2.96	5.04	4.98	6.17	5.99	+.18

TABLE 2.—*Atomic ratios calculated from selected post-1870 analyses of thomsonite cited by Hey, 1932*

[Numbers refer to Hey, 1932, table 2, p. 58-64]

| No. | Ca(+Mg) | Na(+K) | (Ca+Na) | Al | Si | H₂O | | |
						Determined	Calculated	Difference
24a	1.59	1.58	3.17	4.76	5.24	5.52	5.56	−0.04
29	1.56	1.30	2.86	4.64	5.40	5.42	5.20	+.22
32	1.94	1.04	2.98	5.04	5.04	6.23	5.89	+.34
33	1.98	1.10	3.08	5.06	4.94	6.00	6.05	−.05
45	1.96	1.04	3.00	5.03	4.98	6.08	5.94	+−.14
47	1.92	1.16	3.08	4.78	5.16	6.03	5.96	+.07
49	2.04	1.01	3.05	5.02	4.91	6.05	6.11	−.06
54	1.84	1.10	2.94	4.80	5.20	5.98	5.70	+.28
58	1.94	1.10	3.04	4.95	5.05	5.81	5.95	−.14
64	1.94	.91	2.85	4.93	5.11	5.73	5.76	−.03
66	1.18	2.18	3.36	4.67	5.37	6.54	5.13	+1.41
69	1.58	1.62	3.20	4.72	5.26	5.08	5.57	+.49
71	1.64	1.30	2.94	4.57	5.43	5.84	5.40	+.44
72	1.68	1.06	2.74	4.78	5.22	5.64	5.26	+.38
76	1.73	1.06	2.79	4.83	5.24	5.71	5.38	+.33
78	1.68	1.21	2.89	4.62	5.40	5.68	5.41	+.27
79	1.68	1.14	2.82	4.68	5.36	5.66	5.34	+.32
80	1.54	1.24	2.78	4.50	5.56	5.34	5.09	+.25
81	1.60	1.43	3.03	4.60	5.39	5.68	5.43	+.25
83	1.59	1.36	2.95	4.60	5.42	5.77	5.34	+.43
92a	2.14	.95	3.09	5.02	4.92	6.24	6.30	−.06
94	1.97	1.04	3.01	4.98	5.02	5.90	5.96	−.06
95	1.74	1.05	2.79	4.96	5.02	5.79	5.40	+.39
100	1.64	1.50	3.14	4.61	5.36	5.59	5.60	−.01

ment of Ca by Na, by one method or the other, greatly predominates over the reverse and that replacement of Na by Ca is of relatively little importance in the thomsonites.

The atomic ratios yielded by some analyses of thomsonites are so close to the theoretical values that little replacement of either type is indicated. For example, in No. 15, table 1, none of the atomic ratios deviate more than 0.04 from the theoretical values, and the molecular value for H_2O is 5.95 as compared with 6.00. Other analyses whose atomic ratios, given in tables 1 and 2, are very close to the theoretical values, are Nos. 14, 16, 32, 33, 45, 49, and 94. The Si, Al, and (Ca+Na) values for all the other analyses whose atomic ratios are given in tables 1 and 2 indicate both types of replace-

ment, except for Nos. 8, 11, and 81. In these replacement of CaAl by NaSi is indicated; the (Ca+Na) values of 3.00 and 3.03 indicating that no $Na_2 \rightleftharpoons Ca$ replacement has occurred.

In almost all the analyses in which both types of replacement are indicated, the Si value is usually greater than 5.00 and the Al value is less, indicating that replacement of CaAl by NaSi is more common in thomsonites than replacement of NaSi by CaAl. With respect to $Na_2 \rightleftharpoons Ca$ replacement, 17 of the 40 (Ca+Na) values in tables 1 and 2 are greater than 3.00, indicatng replacement of Ca by Na_2, and 20 are less than 3.00, indicating replacement of Na_2 by Ca. As in most thomsonites replacements of the $NaSi \rightleftharpoons CaAl$ type are of NaSi for CaAl. Thus in some there is dual replacement by Na, but in others there is both replacement of CaAl by NaSi and replacement of Na_2 by Ca, with the replacements offsetting each other to greater or less degree. Although the thomsonites whose atomic ratios are given in tables 1 and 2 differ widely in content of Ca and Na, the sum of the atomic ratios for Ca and Na, (Ca+Na) is quite constant, 3.00 ± 0.20 in all but eight of the analyses (Nos. 3, 4, 5, 66, 72, 76, 80, and 95). In Nos. 76 and 80 the difference is only 0.21 and 0.22, respectively.

The relation between Ca and Na in thomsonites is shown graphically in figure 1. The points representing thomsonites whose atomic ratios for Ca and Na are close to the theoretical 2.00 and 1.00, respectively, cluster closely around the asterisk that represents theoretical thomsonite. A few points fall a very short way along the line representing $Na_2 \rightarrow Ca$ replacement, but more fall along or below the line representing NaSi replacement of CaAl. However, none fall as far along this line as the asterisk representing theoretical faroelite. Even the point representing the average Ca and Na ratios for the five Faroe Islands zeolites cited by Hey (1932)—Nos. 19, 21, 22, 23, and 24a—fall short of this point. Farther out along this line is the point representing the "gonnardite" calculated by Hey (1932) from an analysis of a spherulite made up of thomsonite and gonnardite. The points that fall below the $NaSi \rightarrow CaAl$ replacement line represent thomsonites in which replacement of CaAl by NaSi is accompanied by some replacement of Na_2 by Ca. Most of the points representing the Table Mountain, Colo., thomsonites (Nos. 78, 79, 80, 81, and 83, table 2), fall in this area.

The points representing the relation between Ca and Na in thomsonites that have the highest Na content (Nos. 5, 9, 24a, 66, and 69) fall along a line between the $Na_2 \rightarrow Ca$ replacement and the $NaSi \rightarrow CaAl$ replacement lines. This middle line represents dual replacement: replacement of Ca by Na_2 and of Ca as
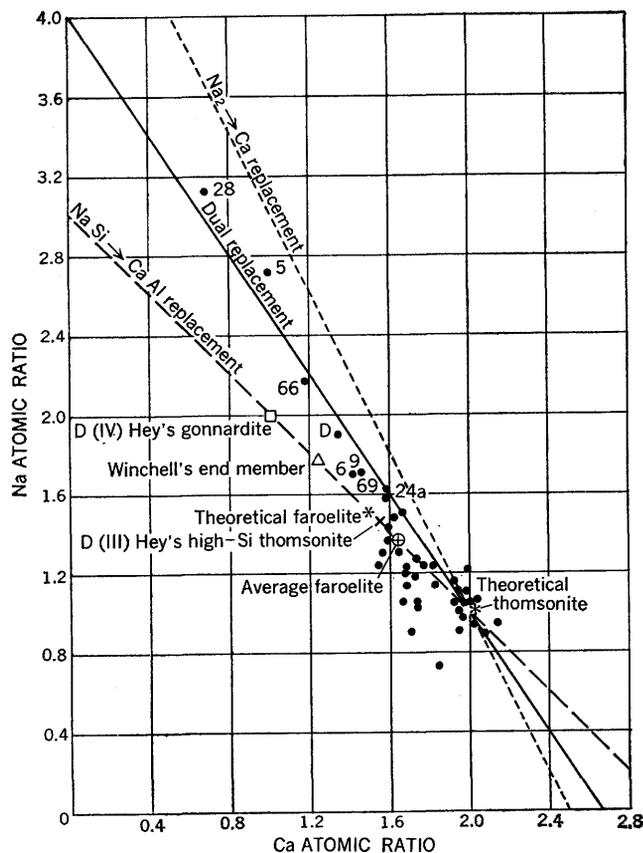

FIGURE 1.—Relation between Ca and Na in thomsonites.

CaAl by NaSi to the same degree. The highest Na ratio in tables 1 and 2 is that in analysis 5, but the highest Na ratio in the analyses cited by Hey (1932) is in analysis 28. The value he gives, 12.50, is for the unit cell, which would be 3.125 in terms of the quarter cell as used in this study. In the same terms the ratio for Ca is only 0.68. The point representing the relation between Ca and Na in this analysis falls considerably farther along the dual replacement line than does the point representing No. 5 which actually falls between the dual replacement line and the $Na_2 \rightarrow Ca$ line. Analysis 28 is cited by Hey as that of a thomsonite, although it had been earlier considered to be that of a mesolite. It was not included in table 2 because of its age (1836).

The relation between Ca and H_2O in thomsonites is shown graphically in figure 2. Although thomsonites that have the same Ca ratio may differ greatly in H_2O content, the points in figure 2 do show a general downward trend in H_2O content with decrease in Ca. In general, analyses having high Ca contents tend to have high H_2O contents, and analyses having low Ca contents tend to have low H_2O contents, except for analyses 1, 4, 6, and 66, in which H_2O is very high. The points representing these analyses fall completely outside the pattern made by the other points.

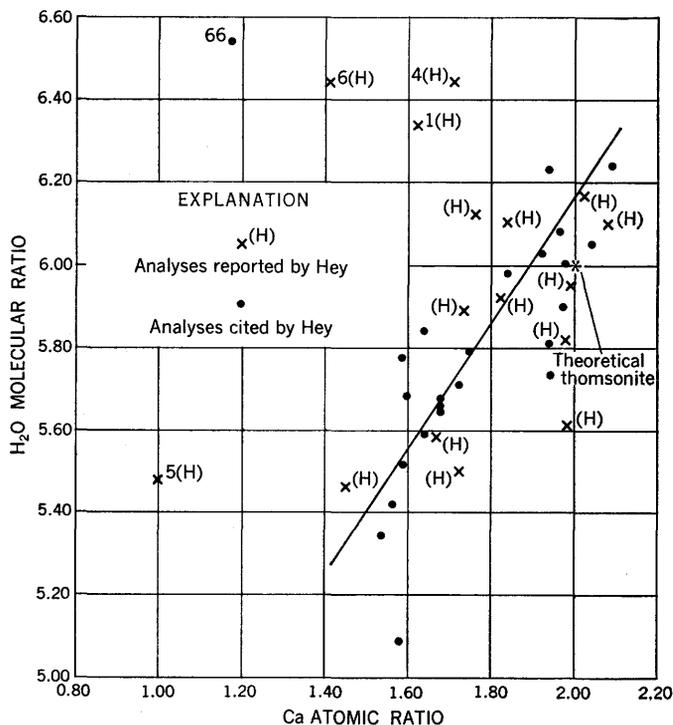FIGURE 2.—Relation between Ca and H_2O in thomsonites.

GONNARDITE

$Na_{2.0}Ca_{1.0}Al_{4.0}Si_{6.0}O_{20} \cdot 7\ H_2O$

Five analyses of gonnardite were published by Meixner, Hey, and Moss (1956), including two (D and

E) that Hey had published in 1932 as an analyses of gonnardite-thomsonite spherules. The outer part of the spherules was described as thomsonite, and the inner part as gonnardite. When the analyses were republished as analyses of gonnardite, no explanation was given as to why analyses originally published as analyses of a composite sample were republished 24 years later as analyses of a single mineral. In 1932 Hey had prorated the constituents found in these analyses between a high-silica thomsonite and hypothetical gonnardite on the basis of assumed compositions and of the proportion of each estimated to be present in the spherule analyzed. The half-cell atomic ratios for this calculated gonnardite, D(IV), are given in table 3. Also given in table 3 with their atomic ratios, are analyses A, B, C, and D of Meixner, Hey, and Moss (1956), two other analyses of gonnardite from the literature, and three recent analyses of high-Na mesolite. The Bulgarian material (Kostov, 1958) analyzed was called "gonnardite (with thomsonite?)." The analysis of the material from Norway is an old one by Paijkull (1874). This material was originally called ranite, but Mason (1957) recently identified it as gonnardite. The analyses of high-Na mesolites given in the last three columns of table 3 indicate compositions very similar to that of gonnardite or high Na thomsonite.

The relation between the atomic ratios of Ca and Na given in table 2 is shown graphically in figure 3. Also shown in figure 3 is the relation between Ca and Na in

TABLE 3.—*Analyses of gonnardites and high-Na mesolites, and their atomic ratios*

[In order of increasing Na_2O content]

| | Gonnardites | | | | | | | High-Na mesolites | | |
	D	D(IV)	C	1	2	A	B	3	4	5
Composition (percent)										
SiO_2	41.85	----------	42.75	42.71	39.21	42.80	43.20	40.03	41.15	40.59
Al_2O_3	27.02	----------	27.36	30.16	31.79	28.15	27.90	27.88	29.49	29.69
CaO	9.29	----------	7.77	6.25	5.07	4.26	3.61	6.03	5.33	5.06
Na_2O	7.25	----------	8.15	9.50	11.55	12.65	13.16	10.05	11.02	11.00
K_2O	n.d.	----------	.15	----------	----------	.13	Trace	.40	.25	.51
H_2O	14.37	----------	13.44	[1] 11.70	11.71	11.85	11.74	[2] 11.10	13.52	13.58
Total	99.78	----------	99.62	[3] 100.50	[4] 99.90	99.84	99.61	[5] 100.29	100.76	100.43
Atoms per half cell (20 oxygens)										
Si	5.64	5.8	5.69	5.52	5.18	5.62	5.67	5.48	5.45	5.41
Al	4.29	4.2	4.29	4.59	4.95	4.36	4.32	4.50	4.60	4.66
(Ca+Mg)	1.34	1.0	1.11	[3] .90	.72	.60	.51	.92	.76	.72
(Na+K)	1.89	2.0	2.12	2.37	2.96	3.24	3.35	2.73	2.86	2.92
(Ca+Na)	3.23	3.0	3.23	3.27	3.68	3.84	3.86	[5] 3.65	3.62	3.64
H_2O (determined)	6.46	----------	5.97	4.85	5.16	5.19	5.14	5.07	5.97	6.03
H_2O (calculated)	5.91	----------	5.45	5.07	5.12	5.04	4.88	5.49	5.14	5.08
Difference	+.55	----------	+.54	−.22	+.04	+.15	+.26	−.42	+.83	+.95

[1] Includes 0.45 H_2O-.
[2] Includes 3.12 H_2O-.
[3] Includes 0.18 MgO (0.04 Mg atomic ratio).
[4] Includes 0.57 Fe_2O_3.
[7] Includes 0.85 Fe_2O_3, 0.59 FeO, 0.22 MgO (0.04 Mg atomic ratio) and 0.02 TiO_2.

LOCALITY AND REFERENCE FOR ANALYSES IN TABLE 7

D. Chaux de Bergonne, France, Meixner, Hey, and Moss, 1956, p. 266.
D(IV). Hypothetical composition of gonnardite, calculated by Hey (1932, p. 117) from D.
C. Aci Castello, Sicily, Meixner, Hey, and Moss, 1956, p. 266.
1. Bourgas Spa, Bulgaria, Kostov, 1958, p. 16, no. 1.
2. Langesundsfjord, Låven, Norway, Dana, 1892, p. 609 (ranite).

A. Klöck, Styria, Meixner, Hey, and Moss, 1956, p. 266.
B. Aci Trezza, Sicily, Meixner, Hey, and Moss, 1956, p. 266.
3. Rio Cambone, Montiferro, Sardinia, Deriu, 1954, p. 42.
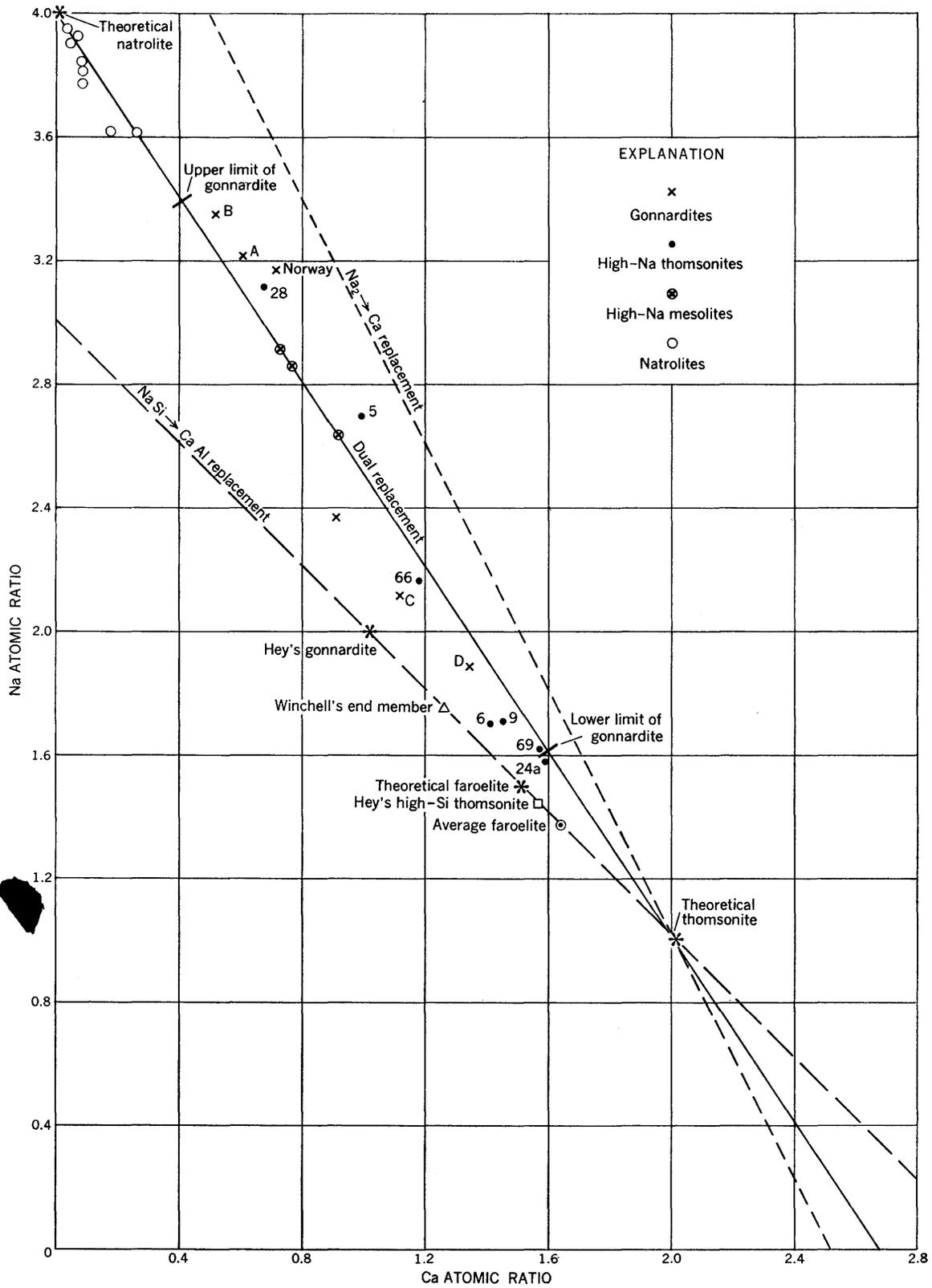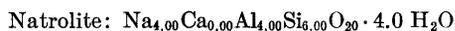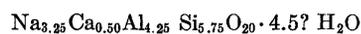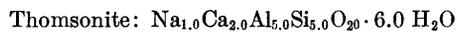4, 5. Kladno, Bohemia, Antonin, 1942, p. 11.

FIGURE 3.—Relation between Ca and Na in gonnardites, and high-Na thomsonites and mesolites.

the high-Na thomsonites given in tables 5 and 6, Nos. 1, 5, 6, 9, 24a, and 66. The relation between Ca and Na in No. 28, which had the highest Na content of the thomsonites cited by Hey (1932), is also shown in figure 4. The material represented by this analysis had previously been called mesolite. The points representing gonnardites intermingle with points representing high-Na thomsonites and mesolites, and all the points fall close to and along the line representing dual replacement, in equal amounts, of Ca by Na_2 and Ca as CaAl by NaSi. On the other hand, the point representing the relation between Ca and Na in the gonnardite D(IV), calculated by Hey from analysis D falls on the line representing NaSi→CaAl replacement at a point equivalent to 50 percent replacement of the Ca in thomsonite as CaAl, and a step beyond the point representing theoretical faroelite, which is equivalent to a replacement of 25 percent of the Ca in thomsonite as CaAl. The point representing the thomsonite calculated by Hey, D(III), also falls on the NaSi→CaAl replacement line a little below the point representing theoretical faroelite. Thus the points for "gonnardite" and "thomsonite" calculated by Hey from analysis D both fall on the NaSi→CaAl replacement line, whereas the point representing D itself falls much closer to the line representing dual replacement.

The intermingling of points representing the relation between Ca and Na in gonnardites, high-Na thomsonites, and so-called mesolites along the line representing dual replacement of Ca in thomsonite suggest that all these zeolites may belong to an isomorphous series characterized by dual NaSi→CaAl and Na_2→Ca replacement, and that theoretical thomsonite, $Ca_{2.0}Na_{1.0}Al_{5.0}Si_{5.0}O_{20} \cdot 6.0$ H_2O, is the high Ca end member of this series.

A THOMSONITE-GONNARDITE-NATROLITE ISOMORPHOUS SERIES?

Gonnardites and high-Na thomsonites can both be interpreted as derived from normal thomsonsite by dual replacement, to about the same degree of Ca by Na_2, and of CaAl by NaSi. Steps in this dual replacement, starting with thomsonite, are shown in these formulas.

Thomsonite: $Na_{1.0}Ca_{2.0}Al_{5.0}Si_{5.0}O_{20} \cdot 6.0$ H_2O

$Na_{1.75}Ca_{1.50}Al_{4.75}Si_{5.25}O_{20} \cdot 5.5?$ H_2O

$Na_{2.50}Ca_{1.00}Al_{4.50}Si_{5.50}O_{20} \cdot 5.0?$ H_2O

$Na_{3.25}Ca_{0.50}Al_{4.25}$ $Si_{5.75}O_{20} \cdot 4.5?$ H_2O

Natrolite: $Na_{4.00}Ca_{0.00}Al_{4.00}Si_{6.00}O_{20} \cdot 4.0$ H_2O

The atomic ratios for No. 9, table 1, are very similar to those in the second formula, which represents the first step in the replacement. The atomic ratios for

the analyses of gonnardite from Bulgaria and the high-Na mesolite from Sardinia, table 3, are similar to those in the third formula, and the atomic ratios for analysis A and B, table 3, are similar to those in the fourth formula. The Ca-free end member is identical with the formula for natrolite. Points representing the relation between Ca and Na in several natrolite analyses, Nos. 12, 15, 17, 22, and 25 (table 1), fall on or close to the upper end of the line representing dual replacement in figure 3. The gonnardite (B, table 3) having the highest Na content has a Na atomic ratio only 0.26 below the Na atomic ratio in the natrolite having the highest Ca content (No. 25, table 1). The formulas for these two analyses are:

Analysis B, table 3: $Na_{3.35}Ca_{.51}Al_{4.32}Si_{5.67}O_{20} \cdot 5.14$ H_2O

Analysis 25, table 1: $Na_{3.61}Ca_{.27}Al_{4.28}Si_{5.77}O_{20} \cdot 4.37$ H_2O

The sum of the cations (Ca+Na) also agrees closely, 3.86 and 3.88 in B and No. 25, respectively.

The high-Na mesolites given in table 3 may be interpreted as either derived from thomsonite by replacement of 0.40–0.50 CaAl by 0.40–0.50 NaSi, plus replacement of 0.60–0.65 Ca by 1.20–1.30 Na_2, or as derived from mesolite by replacement of about 0.50 CaSi by an equivalent amount of Na_3Al.

Deer, Howie, and Zussman (1963, p. 358–359) give the following ranges in indices of refraction for thomsonite, gonnardite, natrolite, and mesolite:

	Optic axial sign	α	β	γ
Thomsonite	+	1.497–1.530	1.513–1.533	1.518–1.544
Gonnardite	−	1.497–1.506		1.499–1.508
Natrolite	+	1.473–1.483	1.476–1.486	1.485–1.496
Mesolite	+		1.504–1.508	

The following data are available on some high-Na thomsonites whose analyses are given in tables 1 and 2 and on the gonnardites and the high-Na mesolites whose analyses are given in table 3:

Analysis	α	β	γ	Source
High-Na thomsonites				
1	1.511	1.513	1.518	Hey, 1932, p. 54.
5	1.523	1.525	1.527	Do.
6	1.518	1.520	1.528	Do.
9	1.517	1.519	1.526	Do.
24a	1.521	1.523	1.528	Hey, 1932, p. 80.
Gonnardites and high-Na mesolites				
A [1]	1.498		1.502	Meixner, Hey, and Moss, 1956, p. 266.
B [1]	1.497		1.499	Do.
C [1]	1.506		1.508	Do.
D [1]	1.506		1.508	Do.
Norway [1]	1.513		1.515	Mason, 1956.
Sardinia	1.5044	1.5052	1.5067	Deriu, 1954.

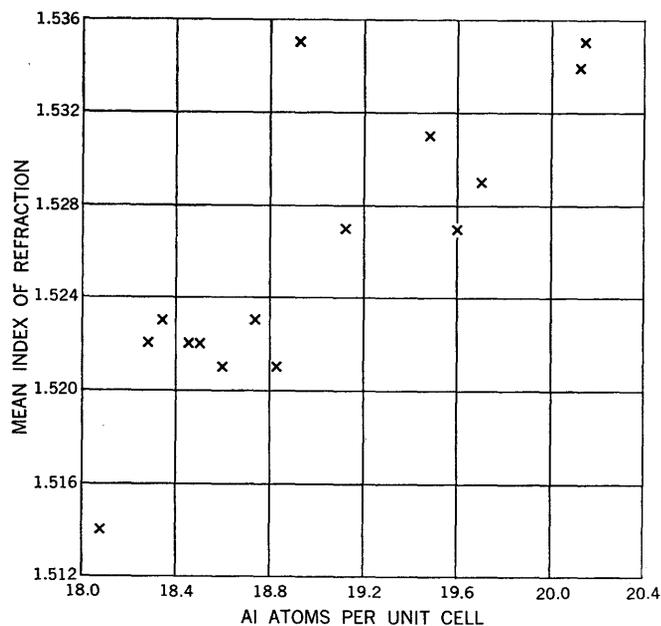[1] The indices of refraction given are not true α and true γ, but α' and γ'.

FIGURE 4. Relation between Al atoms per unit cell and mean index of refraction in thomsonites.
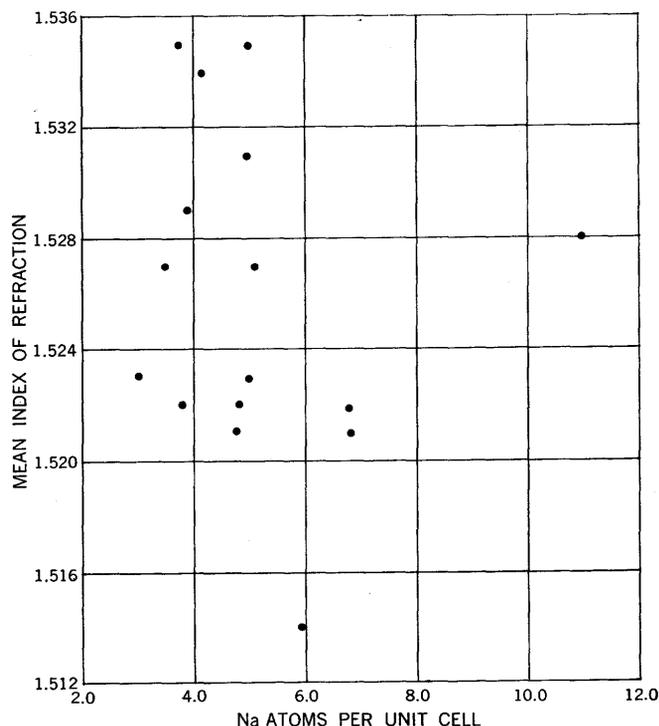

FIGURE 5. Relation between Na atoms per unit cell and mean index of refraction in thomsonites.

Hey (1932) found that the indices of refraction of thomsonite increase with increase in Al, but are little affected by replacement of Ca by Na_2, or vice versa. The relation between Al atoms and Na atoms per unit cell and the mean index of refraction in 16 thomsonites whose analyses were reported by Hey (1932) are shown in figures 4 and 5. The general trend of the points in figure 4 is upward with increase in Al content and mean index of refraction, but the relation is not precise, as some thomsonites having the same Al content may differ considerably in mean index of refraction and vice versa. The location of the points in figure 5 indicates little relation between Na content and mean index of refraction. For example, six thomsonites having about the same number of Na atoms per unit cell, 4.74 to 5.04, range in mean index of refraction from 1.521 to 1.535. Thus the wide ranges in the indices of refraction of thomsonite seem to reflect the wide range in Al content, or conversely, Si content, in thomsonites, rather than variations in Na content or Ca content.

Gonnardites are characterized by varying $NaSi \rightarrow$ CaAl and $Na_2 \rightarrow Ca$ replacement, and should vary considerably in Al content, and, presuming the same relation as in thomsonite, in indices of refraction. The ranges in the indices of refraction for gonnardite given by Deer, Howie, and Zussman are coextensive with the ranges for prime (′) indices of refraction of gonnardite reported by Meixner, Hey, and Moss (1956), and are presumably based on them. Thus the ranges given by Deer, Howie, and Zussman for the indices of

refraction of gonnardite are based on four sets of α' and γ' values. Although these four gonnardites vary widely in Na content, from 1.89 to 3.35 atoms per half cell, they are very similar in Al content, varying only between 4.29 and 4.36 atoms. This is because in D and C, which have the lower Na contents, 1.89 and 2.12 atoms per half cell, replacement of CaAl by NaSi is greater than replacement of Ca by Na_2, whereas in A and B, which have the higher Na contents, 3.24 and 3.35 atoms per half cell, replacement of Ca by Na_2 is greater than replacement of CaAl by NaSi. In all four the amount of NaSi replacement of CaAl is about the same, $0.62+0.70$ CaAl replaced by equivalent amounts of NaSi, but the amount of Ca replaced by Na_2 varies from 0.23 in D and C, to 0.84 in A and 0.86 in B. Consequently all four have about the same Al content and about the same indices of refraction. The relative degree of NaSi or Na_2 replacement is indicated by where the points representing these gonnardites fall with respect to the dual replacement line in figure 3.

The prime (′) indices of refraction reported by Mason (1957) for the Norwegian zeolite that he identified as gonnardite are somewhat higher than those reported for analyses A, B, C, and D, as its higher Al content would suggest, 4.95 atoms per half cell. The indices of refraction reported by Hey for the high-Na thomsonites whose points intermingle with those of gon-

nardite along the dual ·replacement line in figure 3 are also higher than those for gonnardites A, B, C, and D. The high-Na thomsonites are also higher in Al content than these gonnardites, having relatively less replacement of CaAl by NaSi—from 0.24 to 0.46, compared to 0.62 to 0.70 in A, B, C, and D. The indices of refraction for these high-Na thomsonites fall within the ranges of indices for thomsonites. It is probable that further data on the indices of refraction of gonnardite will extend the ranges of the indices of refraction of this zeolite and may show that the ranges of the indices of refraction for gonnardite overlap to some extent those for thomsonite.

The ranges for the indices of refraction of natrolite and mesolite are very narrow, just as their variations in Al content are very small.

The structural similarities between thomsonite, gonnardite, and natrolite are well known. All three zeolites have framework structures in which every (Si, Al)O_4 tetrahedron has each of its oxygens shared with another tetrahedron; linkages to form chains in the z direction are the most prominent. The repeat unit in each chain consists of five tetrahedra and occupies about 6.6A. However, natrolite and thomsonite differ considerably in detail. The structures of thomsonite and natrolite are described by Deer, Howie, and Zussman (1963, p. 361–362) "In thomsonite neighboring chains in the y direction are related by mirror planes (010), but those in the x direction are related by diad axes [010]. The resulting unit cell (orthorhombic *Pnma*) contains four chains * * * . In the structure of natrolite, neighboring chains are related (approximately) by diads only, and this results in a body-centered cell with dimensions similar to those of thomsonite ($a \approx b \approx 13.1$Å) or a face-centered cell with a 18.3, b 18.6Å * * * . The difference between Al and Si tetrahedra and perhaps other deviations from the ideal structure result in orthorhombic (pseudotetragonal) cells for both thomsonite and natrolite. In thomsonite, moreover, such deviations give rise also to a double c parameter ($13.25 \approx 2 \times 6.63$)." The structure of gonnardite is described by Deer, Howie, and Zussman (1963, p. 364) as follows, "Gonnardite has cell parameters similar to those of thomsonite and is assumed to have a similar aluminosilicate framework structure. X-ray fibre photographs of gonnardite are similar to those of thomsonite, and its powder photographs may be confused with those of natrolite (Meixner *et al.*, 1956)." Natrolite is the only one of these three zeolites whose structure has been refined (Meier, 1960).

As the structures of these minerals are similar but differ in detail, it may be that, although analyses suggest a continuous series compositionally, there is a structural change somewhere between thomsonite and

natrolite. Such a change would be analogous to the structural change from dioctahedral to trioctahedral which occurs halfway between muscovite and lepidolite, and which breaks the continuity of the compositional series consisting of muscovite, lithian muscovite, and lepidolite (Foster, 1960).
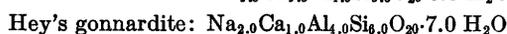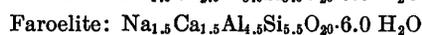
Hey (1932) concluded that the optical properties and X-ray spacings of gonnardite furnish fairly conclusive evidence that it should be regarded as a separate species related to thomsonite perhaps in a manner like that of α- and β-quartz. He tentatively identified gonnardite with metathomsonite, a high-temperature polymorph of thomsonite. The transition from thomsonite to metathomsonite is reversible and the transition temperature is dependent on the water content. The two forms are compositionally the same, except for water content. On the other hand, gonnardite differs in composition from thomsonite, being intermediate in composition between thomsonite and natrolite, and cannot become thomsonite simply by a decrease in temperature and rehydration as metathomsonite does. To obtain thomsonite from gonnardite requires chemical change.

Hey (1955, p. 166) gives the H_2O content of gonnardite as 7 molecules per 20 oxygen atoms. The next year Meixner, Hey, and Moss (1956) give the H_2O content as 6 molecules per 20 oxygen atoms. It has been noted that in natrolite and mesolite the ratio of H_2O molecules to Na ions is 1:1, and that in scolecite and mesolite the ratio of H_2O molecules to Ca ions is 3:1. In thomsonite the ratio of H_2O molecules to Na ions is again 1:1, but the average ratio of H_2O molecules to Ca ions is 2.5:1. Analogously, it would be expected that gonnardites would contain less water than thomsonites, because of the higher Na content and lower Ca content. Also, as they are intermediate in chemical composition between thomsonite and natrolite, they would also be expected to be intermediate in H_2O content. In the analyses of gonnardite given by Meixner, Hey, and Moss, the water content per 20 oxygen atoms varies from 5.35 to 6.1, molecules. In the analyses given in table 3, which includes four of the analyses of Meixner, Hey, and Moss, H_2O varies from 4.85 to 6.46, and averages 5.54 molecules. The average molecular ratio for H_2O in the high-Na thomsonites that fall close to or on the middle line (Nos. 5, 9, 24a, 66, and 69) is 5.42. The average molecular ratio for H_2O in all the analyses whose Ca:Na ratio falls on or close to the dual replacement line in figure 3 is 5.50. For 10 of these 15 analyses the molecular ratio for H_2O is less than 5.50, in three it is close to 6.00, and in two it is more than 6.40. Such H_2O values tend to support the hypothesis that in zeolites that are intermediate in composition between thomsonite and natrolite the

content of H_2O should also be intermediate, and that H_2O contents of 6.00 or 7.00, as assumed in formulas for gonnardites, are too high. In this connection it should be taken into consideration that the average given above is based on total H_2O, as only two of the analyses upon which this average is based reported H_2O-. Therefore the true H_2O content of these zeolites is probably somewhat lower than this average.

FORMULATION

The formula given by Hey (1955) for gonnardite, 2 $[Na_2CaAl_4Si_6O_{20}\cdot 7H_2O]$, can be derived from thomsonite only by unilateral replacement of CaAl by NaSi, as illustrated below:

Thomsonite: $Na_{1.0}Ca_{2.0}Al_{5.0}Si_{5.0}O_{20}\cdot 6.0$ H_2O
Faroelite: $Na_{1.5}Ca_{1.5}Al_{4.5}Si_{5.5}O_{20}\cdot 6.0$ H_2O
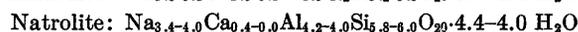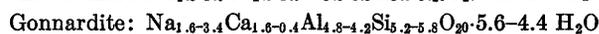Hey's gonnardite: $Na_{2.0}Ca_{1.0}Al_{4.0}Si_{6.0}O_{20}\cdot 7.0$ H_2O

However, the atomic ratios of all the analyzed gonnardites, as well as the atomic ratios of most of the high Na-thomsonites, indicate dual replacement; replacement of CaAl by NaSi, and replacement of Ca by Na_2 to about the same degree. Therefore, the formula given by Hey for gonnardite does not reflect the composition of gonnardite as indicated by analyses, nor does it reflect the great variation in composition found in the materials that have been called gonnardites. Nor does the formula usually given for thomsonite reflect the range in composition found in the thomsonites. The usual thomsonite formula is that of the end member, which bears the same relation to thomsonites in general as phlogopite bears to phlogopites in general, and which bears the same relation to gonnardite that phlogopite bears to biotites.

It is obvious that members of a replacement series that vary in composition and that merge into one another cannot be adequately characterized by formulas that indicate fixed relations between the constituents. For members of such a series only formulas that indicate permissible limits of composition are adequate.

The limits of composition with respect to Na and Ca between thomsonite and gonnardite and between gonnardite and natrolite suggested herein are selected arbitrarily because the analyses indicate considerable continuity, with no natural breaks along the line joining thomsonite and natrolite (fig. 3). The suggested upper limit for thomsonite is at a dual replacement of 0.20 Ca+0.20 Al by 0.20 Na+0.20 Si and of 0.20 Ca by 0.40 Na. Starting with theoretical thomsonite, Na and Ca at this degree of dual replacement are both 1.60. Up to this degree of dual replacement Ca is greater than Na, beyond it Na is greater than Ca. At this degree of replacement of CaAl by NaSi the Al content is 4.80 and the Si content is 5.20. The upper limit of composition

for thomsonite along the line of dual replacement would be, therefore, $Na_{1.60}Ca_{1.60}Al_{4.80}Si_{5.20}O_{20}\cdot 5.60H_2O$. This composition also represents the lower limit of gonnardite. The suggested upper limit of gonnardite is at a dual replacement of 0.80 Ca+0.80 Al by 0.80 Na+0.80 Si and of 0.80 Ca by 1.60 Na. This degree of replacement of CaAl by NaSi results in an Al value of 4.20 and a Si value of 5.80. The upper limit of composition for gonnardite would be $Na_{3.40}Ca_{.40}Al_{4.20}Si_{5.80}O_{20}\cdot 4.40$. H_2O.

The complete formulas with these suggested limits of composition for thomsonite, gonnardite, and natrolite would then be

Thomsonite: $Na_{1.0-1.6}Ca_{2.0-1.6}Al_{5.0-4.8}Si_{5.0-5.20}O_{20}\cdot 6.0-5.6$ H_2O
Gonnardite: $Na_{1.6-3.4}Ca_{1.6-0.4}Al_{4.8-4.2}Si_{5.2-5.8}O_{20}\cdot 5.6-4.4$ H_2O
Natrolite: $Na_{3.4-4.0}Ca_{0.4-0.0}Al_{4.2-4.0}Si_{5.8-6.0}O_{20}\cdot 4.4-4.0$ H_2O

These limits for thomsonite, gonnardite, and natrolite are marked in figure 3. In these formulas the values for H_2O are calculated on the basis of a 1:1 ratio of H_2O to Na and of 2.5:1 ratio of H_2O to Ca, as in thomsonite.

In accordance with these range formulas, analysis No. 24a, table 2, with 1.58 Na and 1.59 Ca comes just within the upper limits for thomsonite, and in 69, table 2, Ca is just within the lower limits for gonnardite. No. 1, table 1, falls well within the limits for thomsonite. No. 9, table 1, and Nos. 28 and 66, table 2, and all the analyses given in table 3 fall within the gonnardite range.

It must be understood that the range formula given above for thomsonite applies only to thomsonites belonging to this dual replacement series. Thomsonite in the NaSi$\rightarrow$CaAl line of replacement would have a range formula reflecting the atomic relations in this line of replacement, such as

$$Ca_{2.0-1.5}Na_{1.0-1.5}Al_{5.0-4.5}Si_{5.0-5.5}O_{20}\cdot 6.0-5.25\ H_2O,$$

which embraces faroelite.

OTHER LINES OF REPLACEMENT

In addition to the two lines of replacement that have been discussed, four other possible lines of replacement are indicated in figure 3. One of these, like the two that have been discussed, is a Ca replacement line, replacement of Ca by Na_2. The other three are all Na replacement lines, continuations of the three Ca replacement lines. However, except for a few points that fall close to theoretical thomsonite, none of the points representing the Ca/Na relations of analyses whose atomic ratios are given in tables 1 and 2 fall along these lines. Replacement of Na by Ca in thomsonites appears to be quite subordinate to replacement of Ca by Na, and replacement of Ca by Na_2 seems to be found most commonly in conjunction with replacement of Ca as CaAl by NaSi, as along the dual replacement line.

CONCLUSION

This study has shown that gonnardites, and several high-Na mesolites, and certain thomsonites that are characterized by dual NaSi-→CaAl and Na_2-→Ca replacements, are all intermediate in composition between thomsonite and natrolite, and suggest an isomorphous series between them. However, differences in optical properties and in structure cast doubt on such an interpretation. Whether all these zeolites are members of an isomorphous series between thomsonite and natrolite or whether only the high-Na thomsonites belong to such a series, and the gonnardites and high-Na mesolites are polymorphic forms, are problems that require more data, especially on their structures, and more study for their clarification.

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