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A further study of analcime solid solutions in the system $NaAlSi_3O_8$-$NaAlSiO_4$-H_2O, with particular note of an analcime phase transformation

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SUMMARY. The stability field of analcime solid solutions in the system $NaAlSi_3O_8$-$NaAlSiO_4$-H_2O has been previously determined by Kim and Burley (1971*a*). These experiments are re-examined with a view to determining the variations of the room-temperature cell parameters of analcime as a function of temperature of synthesis and composition. It is shown from this evidence that most of the analcime solid solutions in these experiments are equilibrium compositions. The increase in the cell dimension of quenched analcime solid solution is found to be 5×10^{-5} Å/°C. It is suggested that birefringence in analcime is induced by low water-pressure relative to total pressure. A phase transition appears to be observed in quenched analcimes of this study and is thought to be the same as that in the Golden analcime reported by Yoder and Weir (1960).

THE mineral analcime is classified chemically and structurally as a zeolite. In common with these minerals it has a very open structure. The structure of analcime (Taylor, 1930) is one of the most unusual known, with sixteen sodium atoms distributed over twenty-four sites. Chemically it has a wide range of composition. Petrologically it has an unusually wide range of occurrence, crystallizing authigenically, being found in the zone of diagenesis, occurring in the zeolite facies of metamorphism, being found commonly in alkaline igneous rocks, and is also reported to crystallize directly from igneous melts at high pressures associated with mantle conditions (Pearce, 1970; Ferguson and Edgar, 1978; Woolley and Symes, 1976). In this respect it is quite different both from other zeolites and also its potassium analogue leucite, as their formation is strongly inhibited by pressure, and their fields of stability disappear at moderate to low pressures. Thus an understanding of analcime mineralogy and chemistry is an invaluable background to understanding its petrological occurrence.

A further intention of the present study is to examine the equilibrium relationships of analcime solid-solutions which are well known to have an extensive range of composition both in synthetic and natural occurrences. The data of Kim and Burley (1971*a*) is re-examined and new data recently obtained is discussed, shedding light on the manner in which analcime cell parameters vary with composition. An increase in the cell dimension of quenched analcime, which is possibly due to disorder phenomena, is noted, as well as a possible quenched high-pressure polymorph. This phase transition is perhaps related to that reported by Yoder and Weir (1960) occurring in analcime from Golden, Colorado.

All of the synthetic analcimes studied in this work have been taken from the run products of our previous work (Kim and Burley, 1971*a*). Lattice parameters of these analcime solid solutions have been determined using the method of Saha (1959), i.e. measuring $\Delta 2\theta$ (Anl_{639}-Si_{331}) using Cu-$K\alpha$ radiation. Each of the $\Delta 2\theta$ values presented in the tables is an average of from 15 to 30 measured values. It is believed that the errors of the $\Delta 2\theta$ measurement are all within ±0.02°, however, most of them are within ±0.01°. Accordingly, the unit cell edges given in the table are believed correct to ±0.003 Å. Most are correct to within 0.002 Å. The experimental data are sorted and classified on the basis of two factors, run-pressure and phase association, and are presented in four tables (Tables I-IV). For information on the physical conditions of the runs see Kim and Burley, 1971*a*. Negligible to trace amounts of birefringent cryptocrystalline material were sometimes observed in the run products; this is considered to be a quench product from the vapour phase and is neglected. The analcime crystals synthesized in the runs are mostly trapezohedral, a few are cubic and somewhat rounded. Grain sizes are mostly within the range 0.05-0.7 mm, the most frequent being about

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Table I. Lattice Parameters of Analcime Solid Solutions (of various composition), coexisting solely with water-vapour phase, synthesized at P_{H_2O} = 2 Kb.

Run No.	Anhydrous Composition of Starting Materials: Weight %		Mole Ratio	Experimental Condition		Lattice parameter	2θ(CuKα) Anl_{639} $-2θSi_{331}$
	Ab	Ne	SiO_2	Press.Kb	Temp.°C	a , Å	Δ2θ, Degree
240	64.8	35.2	4.00	2.02	403	13.716	1.756
245	64.8	35.2	4.00	2.02	358	13.719	1.737
247	89.7	10.3	5.30	2.02	311	13.676	2.024
248	49.2	50.8	3.37	2.02	311	13.739	1.601
256	57.0	43.0	3.67	1.99	444	13.727	1.678
257	49.2	50.8	3.37	1.99	444	13.736	1.620
263	89.7	10.3	5.30	2.04	277	13.675	2.033
264	69.1	30.9	4.19	2.04	277	13.707	1.814
265	64.8	35.2	4.00	2.04	277	13.715	1.760
266	89.7	10.3	5.30	2.04	256	13.674	2.039
267	64.8	35.2	4.00	2.04	256	13.715	1.763
269	69.1	30.9	4.19	2.04	300	13.712	1.780
270	64.8	35.2	4.00	2.04	300	13.718	1.743
271	49.2	50.8	3.37	2.04	300	13.737	1.615
277	104.9	-4.9	6.37	2.02	305	13.649	2.210
294	57.0	43.0	3.67	2.02	506	13.725	1.693
363	57.0	43.0	3.67	2.01	602	13.729	1.667
367	57.0	43.0	3.67	2.01	545	13.726	1.686
583	49.2	50.8	3.37	2.00	472	13.739	1.598
605	100.0	0.0	6.00	2.01	303	13.659	2.141
606	54.7	45.3	3.58	2.01	303	13.732	1.645
608	43.5	56.5	3.18	2.01	379	13.749	1.534
612	43.5	56.5	3.18	2.01	420	13.745	1.562
616	49.2	50.8	3.37	2.01	496	13.739	1.597
617	64.8	35.2	4.00	2.04	169	13.712	1.780
618	59.8	40.2	3.79	2.04	169	13.718	1.742
624a	76.7	23.3	4.56	2.04	347	13.701	1.853
625	49.2	50.8	3.37	2.04	347	13.739	1.602
626	43.5	56.5	3.18	2.04	347	13.745	1.559
632	76.7	23.3	4.56	2.04	233	13.696	1.889
633	64.8	35.2	4.00	2.04	233	13.714	1.768
634	59.8	40.2	3.79	2.04	233	13.719	1.734
635	54.7	45.3	3.58	2.04	233	13.728	1.670
640	76.7	23.3	4.56	2.04	200	13.695	1.895
641	64.8	35.2	4.00	2.04	200	13.710	1.798
642	59.8	40.2	3.79	2.04	200	13.720	1.728
643	54.7	45.3	3.58	2.04	200	13.726	1.690
663	54.7	45.3	2.58	1.97	284	13.729	1.665
679	70.7	29.3	4.26	1.97	358	13.708	1.806
684	64.8	35.2	4.00	1.97	390	13.715	1.760
685hn	39.3	60.7	3.04	1.97	390	13.750	1.525
708a	64.8	35.2	4.00	2.01	413	13.717	1.748
709n	39.3	60.7	3.04	2.01	413	13.750	1.522
719	76.7	23.3	4.56	2.01	300	13.701	1.857
720	43.5	56.5	3.18	2.01	300	13.743	1.569
727	100.0	0.0	6.00	2.01	250	13.659	2.141
729	100.0	0.0	6.00	2.01	250	13.658	2.150
730	49.2	50.8	3.37	2.01	250	13.737	1.611
804	100.0	0.0	6.00	2.03	249	13.657	2.155
808h	43.5	56.5	3.18	2.03	249	13.740	1.592
876	49.2	50.8	3.37	2.00	194	13.738	1.607
878	49.2	50.8	3.37	2.00	194	13.735	1.624

Footnote:

The symbols a, n, h of the end of run numbers denote respectively the trace amounts of albite, nepheline, nepheline hydrate I, coexisting with analcime and vapour.

Table II. Lattice Parameter of Analcime Solid Solutions (of various composition), coexisting solely with water-vapour phase, synthesized at P_{H_2O} ≈ 5.15 Kb.

Run No.	Anhydrous Composition of Starting Materials: Weight %		Mole Ratio	Experimental Condition		Lattice Parameter	2θ(CuKα) Anl_{639} $-2θSi_{331}$
	Ab	Ne	SiO_2	Press.Kb	Temp.°C	Å	2θ,degree
308	49.2	50.8	3.37	5.36	462	13.736	1.618
311	49.2	50.8	3.37	5.36	537	13.737	1.614
359	57.0	43.0	3.67	5.29	645	13.728	1.674
429	64.8	35.2	4.00	5.12	468	13.717	1.747
497	64.8	35.2	4.00	5.10	277	13.711	1.787
500	64.8	35.2	4.00	5.10	245	13.713	1.772
518Z	89.7	10.3	5.30	5.10	272	13.675	2.036
519	54.7	45.3	3.58	5.10	272	13.730	1.661
556	100.0	0.0	6.00	5.10	299	13.659	2.141
570	64.8	35.2	4.00	5.14	178	13.713	1.778
573	54.7	45.3	3.58	5.14	225	13.726	1.689
597	54.7	45.3	3.58	5.23	626	13.732	1.646
652	43.5	56.5	3.18	5.24	375	13.746	1.554
653	100.0	0.0	6.00	5.24	289	13.660	2.139
654	87.7	12.3	5.17	5.24	289	13.679	2.004
655	49.2	50.8	3.37	5.24	289	13.735	1.623
816	43.5	56.5	3.18	5.12	463	13.746	1.550
820	43.5	56.5	3.18	5.12	419	13.746	1.549
847	64.8	35.2	4.00	5.15	220	13.711	1.786
848	49.2	50.8	3.37	5.15	220	13.737	1.612
850	89.7	10.3	5.30	5.15	295	13.671	2.062
851a	76.7	23.3	4.56	5.15	295	13.705	1.830
854	76.7	23.3	4.56	5.15	251	13.695	1.899

Footnote: The symbols, a, and Z, of the end of run number denote respectively the trace amounts of albite and zeolite species P coexisting with analcite and vapour.

Table III. Lattice Parameter of Analcime Solid Solutions coexisting with water vapour and solid phase or phases (albite, nepheline, or nepheline hydrate I), synthesized at P_{H_2O} = 2 Kb.
Abbreviations and symbols: Ab = albite, Ne = nepheline,
N-hI - nepheline hydrate I,
. = small amount, and
.. = very small amount or trace amount.

Run No.	Anhydrous Composition of Starting Materials		Experimental Condition		Lattice Parameter	2θ(CuKα) Anl_{639} -2θ Si_{331}	Phase or Phases coexisting with Analcite & Vapour
	Ab	Ne	Press Kb.	Temp. °C	a, Å	2θ , degree	
239	70.7	29.3	2.02	403	13.721	1.722	..Ab
244	84.0	16.0	2.02	358	13.686	1.960	..Ab
246	35.4	64.6	2.02	358	13.746	1.550	..N-hI
249	32.3	67.7	2.02	311	13.749	1.532	..N-hI
250	29.1	70.9	2.02	298	13.749	1.532	.N-hI
258	42.3	57.7	1.99	444	13.743	1.573	..Ne
292	66.9	33.1	2.02	506	13.719	1.735	..Ab
293	64.8	35.2	2.02	506	13.720	1.730	..Ab
363	57.0	43.0	2.01	602	13.729	1.667	..Ab
368	49.2	50.8	2.01	545	13.736	1.622	..Ne
577	76.7	23.3	2.00	389	13.701	1.856	..Ab
578	29.1	70.9	2.00	389	13.751	1.520	.N-hI
582	64.8	35.2	2.00	472	13.716	1.756	..Ab
607	21.2	78.8	2.01	303	13.749	1.533	.N-hI
609	35.4	64.6	2.01	379	13.748	1.535	.N-hI
610	21.2	78.8	2.01	379	13.754	1.500	N-hI
613	35.4	64.6	2.01	420	13.750	1.527	.Ne
623	87.7	12.3	2.04	347	13.680	1.997	..Ab
624	76.7	23.3	2.04	347	13.701	1.853	-
636	29.1	70.9	2.04	233	13.752	1.514	.N-hI
666	64.8	35.2	1.97	451	13.715	1.760	..Ab
685	39.3	60.7	1.97	390	13.750	1.525	..N-hI+..Ne
708	64.8	35.2	2.01	413	13.717	1.748	..Ab
709	39.3	60.7	2.01	413	13.750	1.522	..Ne
721	39.3	60.7	2.01	300	13.747	1.546	..N-hI
808	43.5	56.5	2.03	249	13.740	1.592	.N-hI
858	59.8	40.2	2.02	585	13.725	1.693	..Ab
859	54.7	45.3	2.02	585	13.733	1.639	-

Table IV: Lattice Parameter of Analcime Solid Solution coexisting with water vapour and solid phase or phases (albite, nepheline, or nepheline hydrate I), synthesized at P_{H_2O} = 5.15 Kb.
Abbreviations and symbols: Ab = albite, Ne = nepheline,
N-hI = nepheline hydrate I,
. = small amount, and
.. = very small amount or trace amount.

Run No.	Anhydrous Composition of Starting Materials		Experimental Condition		Lattice Parameter	2θ(CuKα) Anl_{639} -2θ Si_{331}	Phase or Phases coexisting with Analcite & Vapour
	Ab	Ne	Press Kb.	Temp. °C	a, Å	2θ , degree	
312	35.4	64.6	5.36	537	13.745	1.558	.Ne
359	57.0	43.0	5.29	645	13.728	1.674	-
360	49.2	50.8	5.29	645	13.735	1.625	.Ne
428	66.9	33.1	5.12	468	13.716	1.755	..Ab
520	84.0	16.0	5.10	349	13.688	1.944	.Ab
521	42.3	57.7	5.10	349	13.744	1.564	..N-hI
522	35.4	64.6	5.10	349	13.744	1.562	.N-hI
524	35.4	64.6	5.10	482	13.747	1.547	.Ne
525	29.1	70.9	5.10	482	13.750	1.522	.Ne
559	87.7	12.3	5.10	338	13.680	1.997	.Ab
588	35.4	64.6	5.08	437	13.745	1.560	.Ne
589	29.1	70.9	5.08	437	13.751	1.519	.Ne
592	64.8	35.2	5.08	496	13.716	1.757	..Ab
596	59.8	28.2	5.23	626	13.724	1.698	..Ab
647	35.4	64.6	5.24	415	13.740	1.593	..N-hI
648	29.1	70.9	5.24	415	13.751	1.518	..N-hI
651	76.7	23.3	5.24	375	13.703	1.841	..Ab
817	39.3	60.7	5.12	463	13.748	1.538	..Ne
855	43.5	56.5	5.15	250	13.740	1.590	..N-hI

Table V: Solubility of Albite and Nepheline in Water Vapour

Experimental Condition		Molecular Ratios of Dissolved Solids			Total Solute	Investigator and Starting Materials
Press. bar	Temp. °C	Na_2O	Al_2O_3	SiO_2	Wt%	
400	500	1.00	0.71	8.63	0.0062	Morey & Hesselgesser
1,000	500	1.00	0.90	6.17	0.077	(1951, p. 829)
2,000	500	1.00	0.98	6.10	0.2675	Amelia Albite
7,000	750	1.000	0.932	5.436	5.70	Clark (1966, p.436)
7,600	760	1.000	0.967	5.850	6.70	Determined by Burnham
9,700	700	1.000	0.783	4.890	10.20	$NaAlSi_3O_8$ - Glass
4,900	900	1.000	1.035	1.018	5.30	Clark (1966, p.436)
7,600	780	1.000	0.860	1.000	17.00	Determined by Burnham
8,700	750	1.000	0.922	1.412	31.50	$NaAlSiO_4$ - Glass

0.3 mm. All the analcimes synthesized in the presence of excess water vapour are optically isotropic without exception.

Burley and Freeman (1959) investigated the temperature dependence of quenched analcime's cell dimension. They found no significant change in the quenched analcime cell size as a function of synthesis temperature. During the period of previous work carried out by the authors (Kim and Burley, 1971*a*) it was noticed, however, that a portion of the thermal expansion of analcime did appear to be retained through quenching experiments. It is possible that this frozen-in expansion may be related to disorder in the crystal structure. Mazzi and Galli (1978) have shown recently that every analcime is slightly different from every other analcime. They report a cubic, an orthorhombic, and two tetragonal structures existing. They relate these structures to the Al-Si ordering caused by differing occupancies of the Na site. Burley and Freeman (1959) in their study of temperature-induced variation in analcime used the parameter $\Delta 2\theta_{400\text{-}211}$ of analcime but it appears that the parameter used in this study $\Delta 2\theta$ (Anl_{639}-Si_{331}) Cu-$K\alpha$, first used by Saha (1959) is more sensitive to small changes in lattice parameters.

A contoured diagram of analcime cell parameters has been constructed on the isobaric T-X phase diagram at 2 kb (fig. 1) using data from Table I. Volume increments of quenched analcime parameters may be observed with increasing run-temperatures. A zone of discontinuity joins the two points (340 °C, $\text{Ab}_{74}\text{Ne}_{26}$) and (407 °C, $\text{Ab}_{42}\text{Ne}_{58}$). This discontinuity in the analcime cell parameter is tentatively attributed to a polymorphic phase transition.

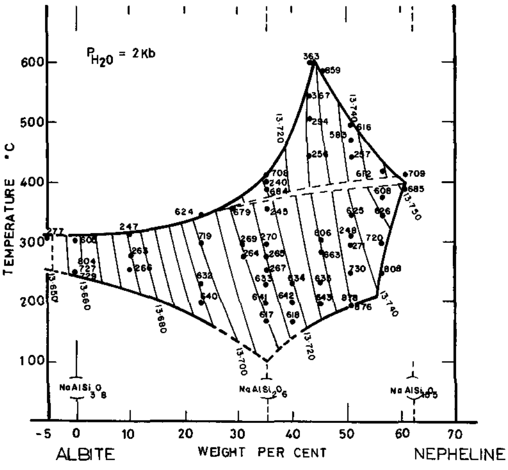

FIG. 1. Contours of constant cell dimension of analcimes coexisting with water vapour at 2 kb as a function of temperature and composition. See Table I for details of the run numbers.

In order to better illustrate the temperature-related cell parameters of analcime and its possible phase transition, fig. 2 has been prepared. The data available in Table I are plotted on a plane diagram with two coordinate axes, one the lattice parameters of analcime and the other run-temperature. The anhydrous composition of each analcime and its corresponding approximate chemical formula derived by Kim and Burley (1971*c*) are given on the diagram. To a first approximation, the relationship of quenched analcime lattice parameter versus run-temperature may be considered a straight line for a given composition. The increase in the cell dimension of quenched low-temperature analcime is about 5×10^{-5} Å/°C depending slightly on its specific composition. A similar linear change in cell parameter of quenched analcime with temperature of formation was noted by Liou (1971) for analcime of idealized composition ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$) and synthesized at 2 kb H_2O pressure, and varying temperatures from 350 to 600 °C. Liou obtained a change in the analcime cell dimension from 13.713 to 13.736. However, it is not possible to synthesize analcime of composition $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ in this temperature range and pressure (see fig. 7), since under these conditions the composition is in the phase field analcime + albite + vapour. Hence Liou must have also been synthesizing a small amount of albite, and the change in the cell dimension he observed was due to the change in the analcime composition along the phase boundary. It is interesting to note that the change in cell dimensions to be expected under these conditions is 1.714 to 1.732 (see fig. 2), very close to what in fact Liou observed. Pertsowsky (1973) also reported a variation in cell dimension with temperature for analcimes of widely varying compositions, synthesized at a pressure estimated to be between 800 and 1000 bar water pressure. However, a similar criticism of Pertsowsky's work can be made, as was made of Liou's, since some of Pertsowsky's syntheses were made in the field of analcime + nepheline hydrate + vapour, some in the field of analcime + albite + vapour, and some in the field of analcime + vapour. The composition of his analcimes were therefore definitely not what he assumed them to be.

The increase in the quenched-cell dimension of the high-temperature form of analcime shows greater variability depending on its composition, see fig. 2. At approximately 376° at 2 kb there is an apparent negative difference in the unit cell volume between the low- and high-temperature forms of analcime of composition $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ of 3.5 Å^3, which is about 27 % of the negative volume change reported by Yoder and Weir (1960)

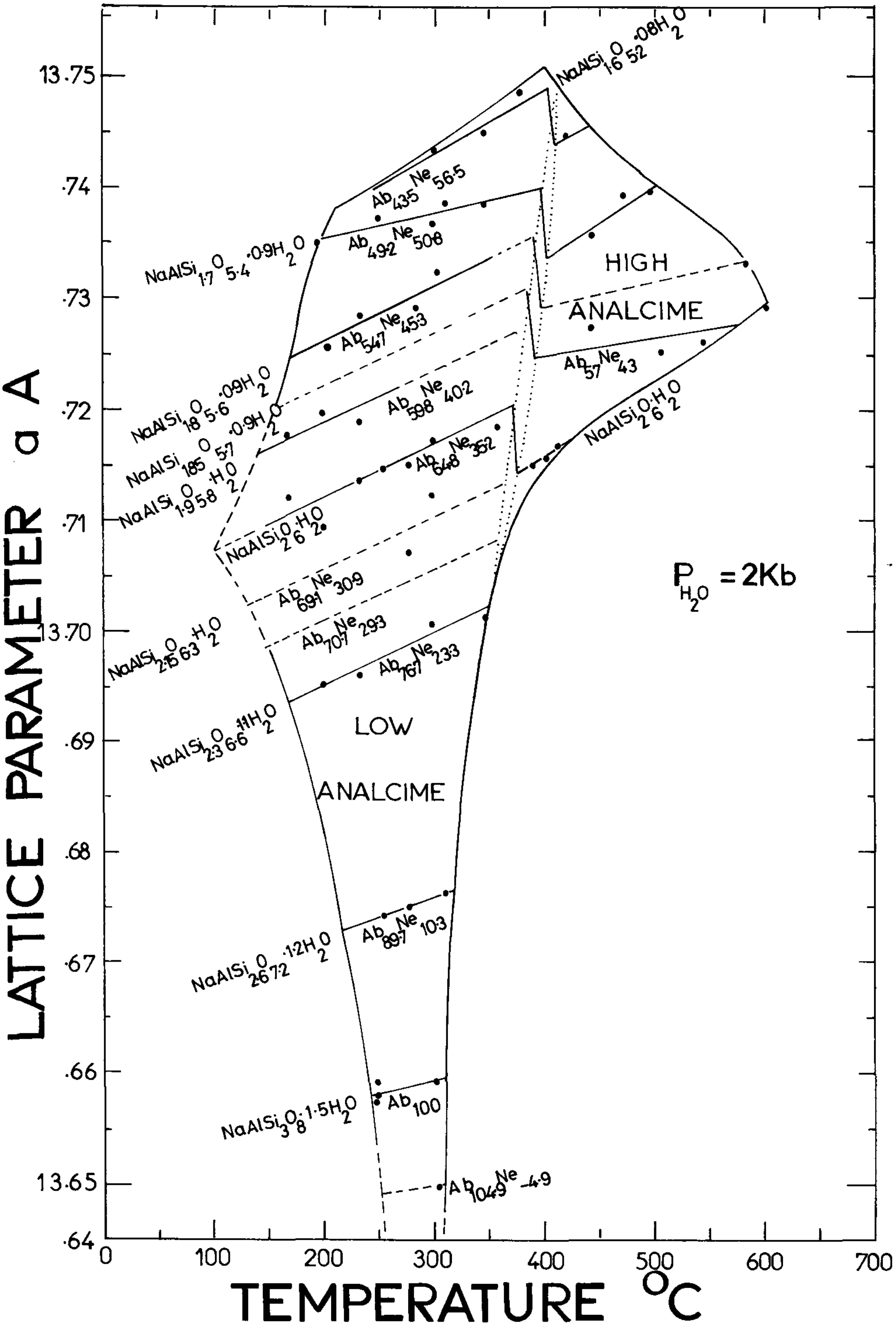

FIG. 2. Constant composition contours of analcime, coexisting with water vapour at 2 kb, as a function of synthesis temperature and cell dimension.

for analcime from Golden undergoing a transition at 8400 atm and 25 °C. Of course, it is to be emphasized that the volume change reported by Yoder and Weir was measured at the conditions of the transition.

It is to be noted that Yoder and Weir felt that the volume discontinuity reported by them could not be evaluated with great precision because it occurred over a finite pressure range. This would be impossible, of course, for a first-order transition, unless there was a two-phase region due to solid-solution effects. Yoder and Weir also felt that the transition noted by them was nonquenchable, but later reported that certain of their analcimes showed birefringence which they thought may be due to lower symmetry induced by the transition. In other words, the transition may have been quenchable. It is difficult to evaluate Yoder and Weir's results, but it is, of course, probable that the nature of the transition varies with the composition of the analcime. Another interesting factor is that Yoder and Weir noted abnormal compressibility (β) in natural analcimes, i.e. $(\frac{\delta\beta}{\delta P})_T > 0$, a property found in only very few substances.

Because of the similarity of Yoder and Weir's results with those of the authors the data of Yoder and Weir have been collated tentatively with the authors' data to produce fig. 3. The negative slope of the P-T curve of the transition, combined with the negative volume change of the transition, requires that the high-pressure analcime have a higher entropy than the low-pressure phase. This somewhat anomalous entropy effect may be correlatable with the anomalous compressibility noted by Yoder and Weir. The transition may also, of course, be complicated by the effect of varying other components, e.g. K_2O, CaO, etc. that occur in natural analcimes, which Yoder and Weir were studying.

It is possible that the volume discontinuity in analcime reported in this study may not be due to polymorphism. The two most likely other causes are: (1) a dehydration reaction; (2) compositional deviation of the analcime from the starting composition due to incongruent solubility of the solid in the water vapour.

The first possibility was tested by measuring the H_2O content of three analcimes synthesized at $P_{H_2O} = 2$ kb by using a technique modified from Kennedy *et al.* (1962), see Kim and Burley (1971*c*) for details. The results were as follows:

(*a*) The H_2O content of analcime $Ab_{64.8}Ne_{35.2}$ ($NaAlSi_2O_6 \cdot H_2O$) was the following: 8.7 wt% at 169 °C, 8.2 wt% at 233 °C, 7.5 wt% at 358 °C, 8.3 wt% at 390 °C and 8.0 wt% at 413 °C.

(*b*) The H_2O content of analcime ($Ab_{49.2}Ne_{50.8}$) was the following: 7.4 wt% at 250 °C, 7.6 wt% at 347 °C, 8.2 wt% at 444 °C and 8.3 wt% at 472 °C.

(*c*) The water content of analcime ($Ab_{43.5}Ne_{56.5}$) was the following: 7.5 wt% at 300 °C, 7.1 wt% at 347 °C, 7.3 wt% at 379 °C and 7.8 wt% at 420 °C.

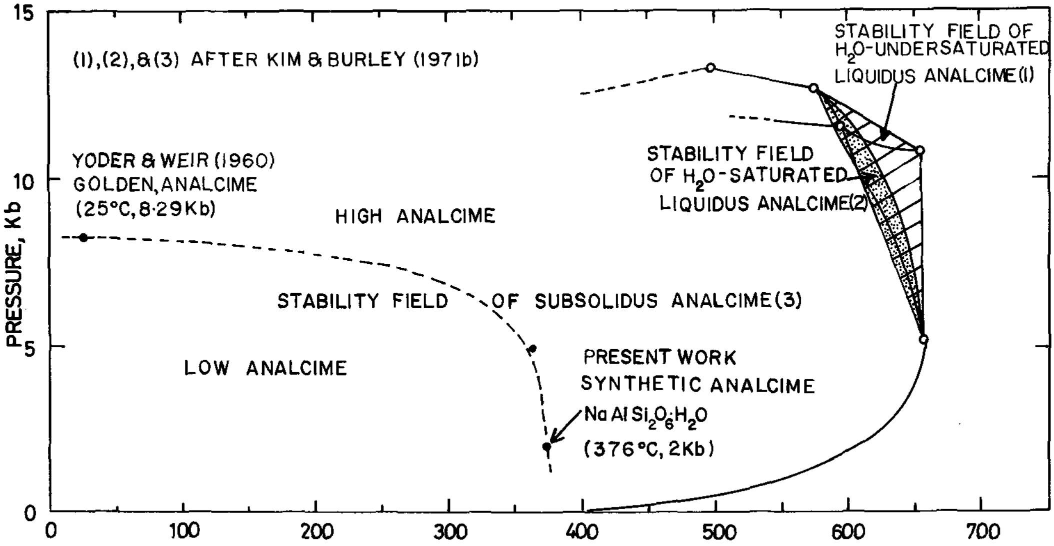

FIG. 3. Stability of low and high analcime ($NaAlSi_2O_6 \cdot H_2O$) as a function of P and T, together with the liquidus relationships from Kim and Burley (1971*b*).

The results show that the water content of analcimes decrease up to the transition temperature. Above the transition temperature the analcimes have an increased water content. It is thus unlikely that the negative volume change experienced at the transition can be explained by this change in water content. On the contrary, it seems necessary to invoke a structural change.

The second possibility that there is incongruent solubility of the solid in the vapour phase, thus changing the composition of the analcime, requires close examination, since no attempt was made during the experiments to determine the quantity of the dissolved solid in the vapour. Table V reports some data taken from the literature pertinent to this problem. It is seen from these data that at pressures between 1 and 7 kb the system $NaAlSi_3O_8$-$NaAlSiO_4$-H_2O is essentially ternary. The data indicates that the dissolved solid in the vapour is only slightly increased in quantity towards $NaAlSiO_4$ relative to the bulk composition. It is believed that the composition of the solid dissolved in the vapour in these experiments is negligibly different from the starting compositions, and cannot therefore be a cause of the discontinuity noticed in the cell dimensions.

Birefringency of synthetic analcimes. Yoder and Weir (ibid.) observed that analcime became birefringent after it had been transformed to a denser form, whereas the quenched denser form observed in this study is completely isotropic, and in fact all of the analcimes synthesized in the presence of excess water appear optically isotropic.

To test the effect of a drier environment, four runs were made without excess water. Two of these runs using analcime ($NaAlSi_2O_6 \cdot H_2O$) as a starting composition were run at 2.03 kb and 300 °C for 27 days, and two runs using analcime ($NaAlSi_3O_8 \cdot 1.5H_2O$) were run at 2.03 kb 249 °C for 27 days. All these runs were without water added. The results are that in the first two runs one-third of the analcime grains show a weak uniform birefringence, whereas in the latter runs all of the analcime grains show weak birefringence. The X-ray powder patterns of all these analcimes show no discernible difference from those made before the experiments.

Klein (1897) and Náray-Szabó (1938) both attributed birefringence in analcime to the loss of water. Klein reported that analcime became birefringent and the degree of its birefringence was increased by the loss of water caused by heat treatment either in a dry atmosphere or in the presence of water vapour. Brögger (1890) pointed out, however, that analyses of Låven eudnophite showed no deficiency in water content. Eudnophite is a birefringent twinned analcime, first described and named by Weibye (1850). Stewart (1941) studied analcime collected from a quarry at Allt a'Mhuillin, Loch Borralan, Assynt, Scotland, and noted the similarity of the optical anomalies of the Allt a'Mhuillin analcime to the Låven eudnophite, and suggested as a conclusion that the optical anomalies of analcime may be due to strain during crystallization. Yoder and Weir (1960) concluded, 'The analcime (Golden, Colorado, USNM84842) exhibiting the transition showed an increase in birefringence after compression, which is attributed either to strain induced by the volume discontinuity or to a possible lower symmetry of the high-pressure form.' Yoder and Weir thought that the transition was not quenchable and did not explain their conclusion that the birefringence could be due to a lower symmetry exhibited by the high-pressure form. It is possible that in fact the transition they noted was partially quenchable. The present authors, of course, are reporting a quenchable transition. The actual nature of the transition may vary somewhat depending on the composition of the analcime being studied. What is certain though is that many analcimes showing birefringence, including those reported in this paper, have not been subjected to conditions appropriate to the transition, although they have undergone some structural modifications. The authors conclude that birefringence in synthetic analcime is attributable to dry compression, possibly resulting in lattice strain. Such analcimes may have the structures reported by Mazzi and Galli (1978).

Equilibrium composition of analcime solid solution. The two isobaric (2 kb and 5.15 kb) sections in the system $NaAlSi_3O_8$-$NaAlSiO_4$-H_2O which had been determined in our previous work (Kim and Burley, 1971*a*) using a bulk-composition method, have been re-examined, using the X-ray composition method of the present study, with especial emphasis on the analcime stability fields.

Coombs and Whetten (1967) have shown that the relationship between the lattice parameter of analcime and its composition in the range of composition from $NaAlSi_{1.5}O_5$ to $NaAlSi_3O_8$ is not strictly linear. Saha (1959) reported that the water content of analcime is linearly proportional to its SiO_2 mole ratio, whereas Kim and Burley (1971*c*) demonstrated, using the techniques of Kennedy *et al.* (1962) with some modification, that the H_2O-content of analcime is generally proportional to its SiO_2/Al_2O_3 mole ratio, but it is not linearly related to either SiO_2 or Al_2O_3.

To incorporate new data reported in this paper and because the relationship between $\Delta 2\theta$ (Anl_{639}-Si_{331}) and the composition of analcime solid solutions is not strictly linear, the X-ray parameter versus composition curves are reconstructed in figs.

4 and 5. The determinative curves have been further classified on the basis of the phases associated with analcime. Each of the five curves is characterized by a unique three-phase assemblage and represents a relationship of the lattice parameter and the composition of analcime solid solution co-existing with one of the other crystalline phases, albite, nepheline, nepheline-hydrate I, and zeolite species P in the presence of excess water vapour. Thus the X-ray composition-determinative curve is no longer a single line, because of the effect of temperature etc., but a zone bounded by several characteristic curves of these differing phase associations. The area enclosed by these five curves represents the lattice parameter-composition relationships of analcime solid solution co-existing solely with water vapour. The present data are in reasonable agreement with a number of previously reported results, particularly with those of Coombs and Whetten (1967), see fig. 6.

Using the X-ray composition-determinative curves shown (figs. 4 and 5), the compositions of the analcime solid solution associated with three of the other phases have been determined from the $\Delta 2\theta$ values given in Tables III and IV and shown in figs. 7 and 8 respectively. The stability fields of analcime solid solution determined firstly by the method of bulk composition and secondly by X-ray parameter determination agree reasonably well with minor exceptions. The minor exception occurs at the phase boundary at 2 kb between albite + analcime + vapour and analcime + vapour (see fig. 7). It appears that reactions in these regions are sluggish, and the structures do not reach equilibrium readily. It is known that natural analcimes of composition $NaAlSi_2O_6 \cdot H_2O$ exsolve albite when heated much above 400 °C. For this reason the authors favour the boundary determined by the bulk-composition method. It may be assumed therefore that generally the analcime solid solutions have assumed their equilibrium compositions, and this confirms the T-X sections determined by Kim and Burley (1971*a*).

Conclusion. It is reported that analcime exhibits unusual, anomalous compressive and thermal changes at elevated pressures and temperature. These changes culminate in a phase transformation. It is probable that this behaviour, which will result in unusual thermodynamic characteristics, explains analcime's unusually widespread occurrence in a variety of geological environments. The phase transformation has been characterized for a variety of compositions at a constant pressure and it is believed correlatable with a transformation reported by Yoder and Weir. The correlation between unit cell parameters and composition for a wide range of analcime solid solutions has been made and used to demonstrate that previous work by Kim and Burley is correct within reasonable error. Birefringence in analcime is believed to be a result of lattice strain caused by relatively dry compressions.

It is probable that natural analcimes are unlikely to show evidence of this phase transition, because there is evidence that analcime appears to re-equilibrate at lower temperatures and pressures somewhat easily (Woolley and Symes, 1976).

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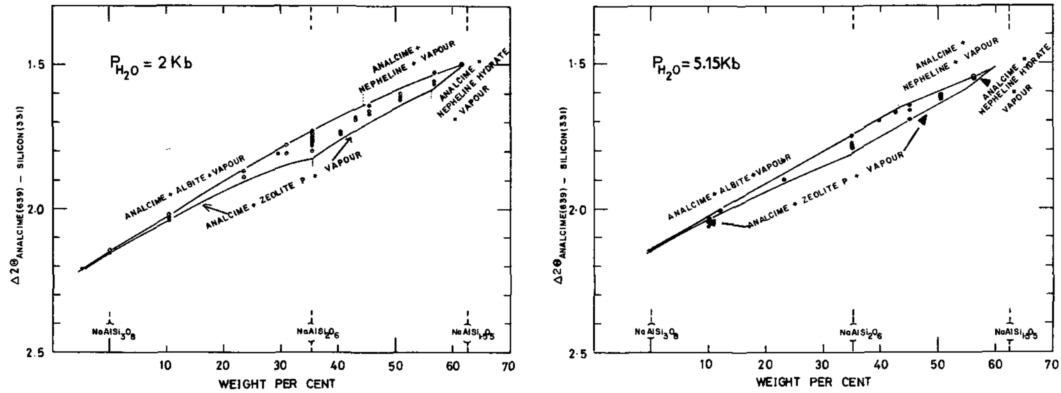


FIGS. 4 and 5. FIG. 4 (*left*). $\Delta 2\theta(Anl_{639}-Si_{331})$ of different analcimes coexisting with water vapour at 2 kb and on the peripheral curves additionally with one of albite, nepheline, nepheline hydrate, or zeolite P. FIG. 5 (*right*). $\Delta 2\theta(Anl_{639}-Si_{331})$ of different analcimes coexisting with water vapour at 5.15 kb and on the peripheral curves additionally with one of albite, nepheline, nepheline hydrate, or zeolite P as a function of composition.

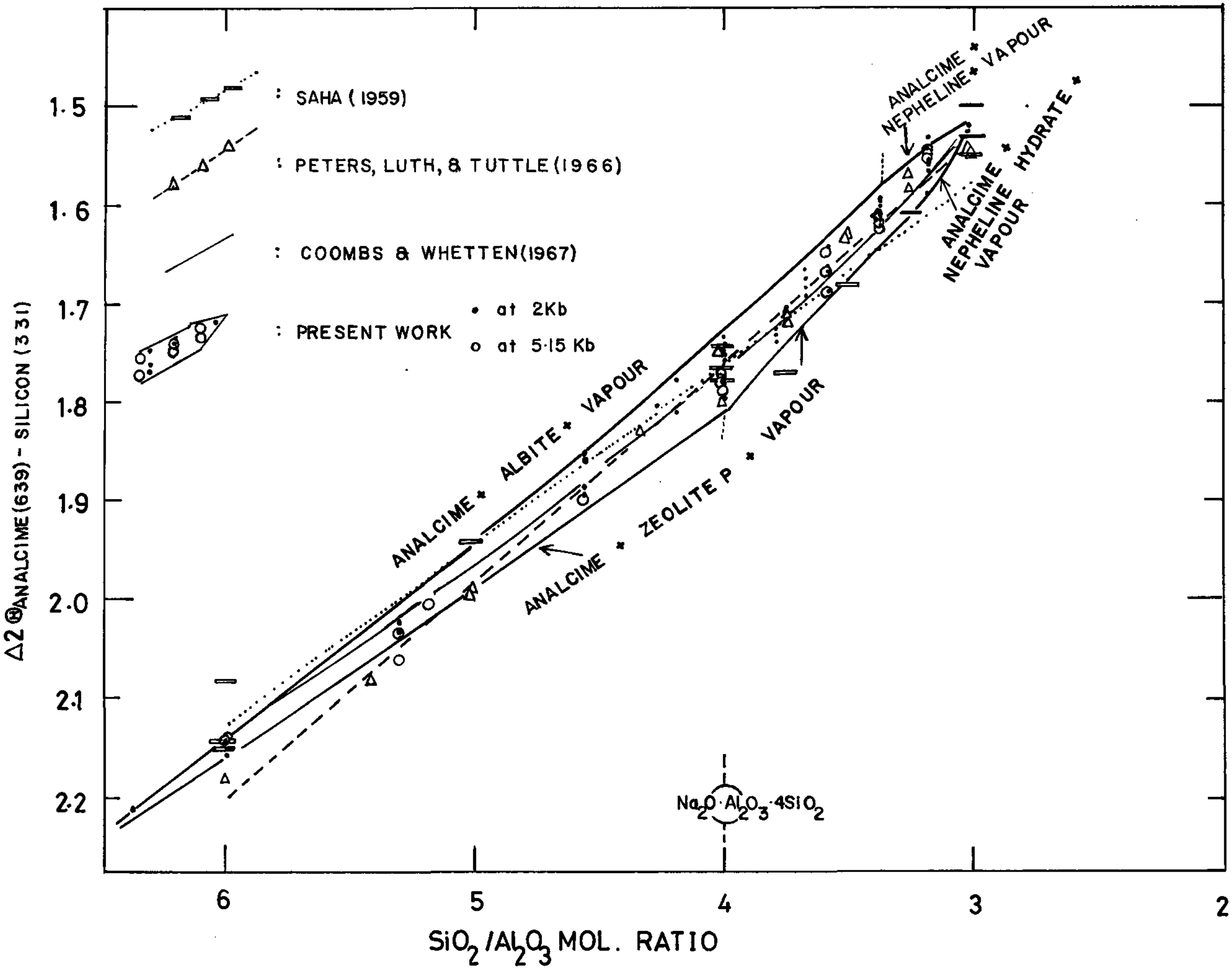
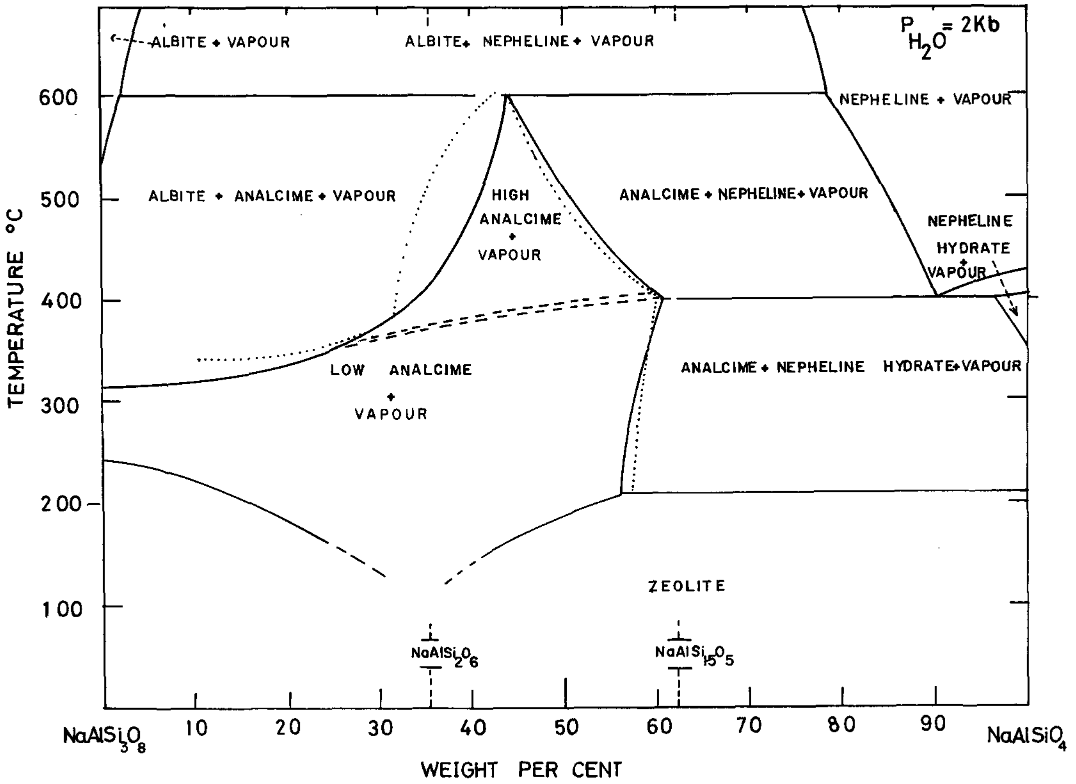
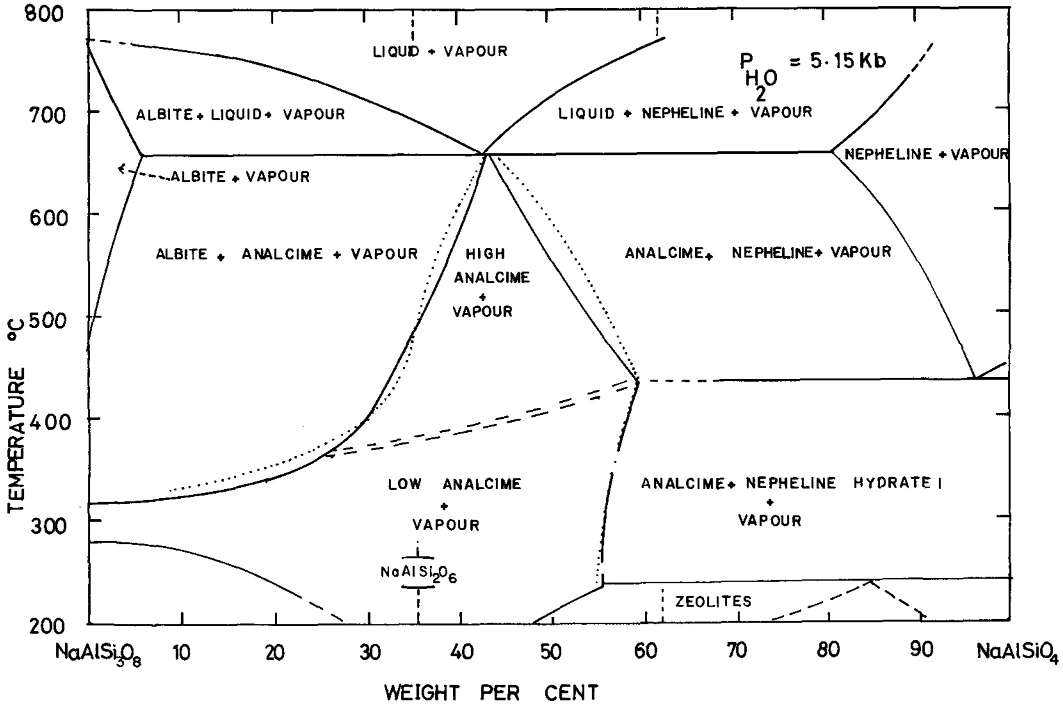


FIG. 6. $\Delta 2\theta(\text{Anl}_{639}\text{–Si}_{331})$ of different analcimes coexisting with water vapour at both 2 and 5.15 kb, and on the peripheral curves additionally one of albite, nepheline, nepheline hydrate, or zeolite P together with data obtained by other workers.


P$_{H_2O}$ = 2Kb
ALBITE + VAPOUR
ALBITE + NEPHELINE + VAPOUR
NEPHELINE + VAPOUR
ALBITE + ANALCIME + VAPOUR
HIGH ANALCIME + VAPOUR
ANALCIME + NEPHELINE + VAPOUR
NEPHELINE HYDRATE + VAPOUR
LOW ANALCIME + VAPOUR
ANALCIME + NEPHELINE HYDRATE + VAPOUR
ZEOLITE
NaAlSi$_2$O$_6$
NaAlSi$_{1.5}$O$_5$
TEMPERATURE °C
100
200
300
400
500
600
NaAlSi$_3$O$_8$
10
20
30
40
50
60
70
80
90
NaAlSiO$_4$
WEIGHT PER CENT


P$_{H_2O}$ = 5·15 Kb
LIQUID + VAPOUR
ALBITE + LIQUID + VAPOUR
LIQUID + NEPHELINE + VAPOUR
ALBITE + VAPOUR
NEPHELINE + VAPOUR
ALBITE + ANALCIME + VAPOUR
HIGH ANALCIME + VAPOUR
ANALCIME + NEPHELINE + VAPOUR
LOW ANALCIME + VAPOUR
ANALCIME + NEPHELINE HYDRATE I + VAPOUR
NaAlSi$_2$O$_6$
ZEOLITES
TEMPERATURE °C
200
300
400
500
600
700
800
NaAlSi$_3$O$_8$
10
20
30
40
50
60
70
80
90
NaAlSiO$_4$
WEIGHT PER CENT

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FIGS. 7 and 8. FIG. 7 (*top*). *T-X* diagram of the system $NaAlSi_3O_8$-$NaAlSiO_4$-H_2O at 2 kb fluid pressure, with phase boundaries determined by bulk composition method (Kim and Burley, 1971*a*) solid line, and by X-ray parameter method (this work) dotted line. FIG. 8 (*bottom*). *T-X* diagram of the system $NaAlSi_3O_8$-$NaAlSiO_4$-H_2O at 5.15 kb fluid pressure, with phase boundaries determined by the bulk composition method (Kim and Burley, 1971*a*) solid line, and by X-ray parameter method (this work) dotted.