THE EFFECT OF TEMPERATURE ON THE LATTICE PARAMETERS OF QUENCHED SYNTHETIC ANALCIME

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ABSTRACT

Mixtures of analcime composition have been crystallized to analcime in the presence of water vapour and at a pressure of fifteen thousand pounds per square inch, and at temperatures of 200°C to 540°C. Most of the runs were of two to eight days' duration. No significant variations in the lattice parameter $2\theta_{400}$–$2\theta_{211}$ of analcime were observed.

INTRODUCTION

The structure of analcime is peculiar in that according to Taylor (1930) it shows a departure from space group principles. Taylor places analcime in the space group *Ia3d*, with sixteen formula units ($NaAlSi_2O_6.H_2O$) per unit cell. He placed the thirty-two silicon and sixteen aluminum atoms randomly at the forty-eight fold (*g*) positions; the sixteen sodium atoms he destributed among the twenty-fourfold (*c*) positions so that, on the average, two thirds of a sodium atom occupies each position. The sixteen water molecules are at the sixteen (*b*) positions, and the ninety-six oxygen atoms are at the ninety-six (*h*) positions. Therefore the structure is not fully ordered.

Kästner (1931) suggested that the structure may be merely pseudocubic, with lower symmetry. He suggests that the space group may be $I4_1/acd$. This space group has most of the systematic absences of the cubic group *Ia3d*. Kästner suggests a structure which closely resembles the cubic one, and in this structure the Si and Al atoms are at nonequivalent positions. The structure is ordered and space group principles are not violated. No recent structural determination of this mineral has been made.

The optical properties of analcime are somewhat ambiguous. Crystals of analcime are often reported to be weakly birefringent with complicated twinning. For a discussion of the birefringence of analcime see Stewart (1941).

If Taylor's analcime structure is correct, it might be possible to cause different degrees of ordering at the Al-Si sites with different temperatures

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of formation. The purpose of this study was to test this hypothesis by synthesizing analcime at different temperatures and observing the changes in cell parameters that may occur.

Previous Work on the Stability of Analcime

There has been a considerable amount of work on the synthesis and stability of analcime. All the work before 1937 has been reviewed by Morey & Ingerson (1937). Yoder (1954) investigated the stability of analcime in the presence of water vapour under high confining pressures and temperatures. His equilibrium curve is shown in Figure 1. Fyfe (1958) has determined the stability of analcime + quartz and his field of equilibrium is also shown for comparison in Figure 1.

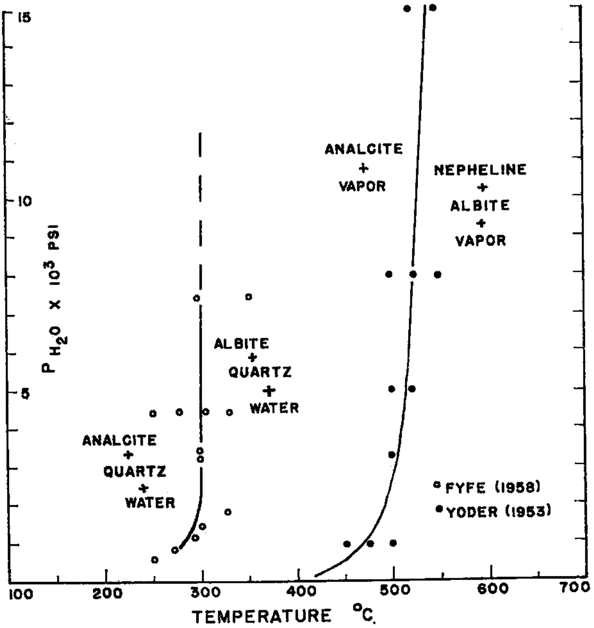

FIG. 1. The stability of analcime for the system analcime + water after Yoder (1954), and the stability of analcime for the system analcime + silica after Fyfe (1958), 168.

It is to be noted that the field of analcime + quartz is more restricted than the field of analcime by itself. Fyfe (*op.cit.*, p. 169) implies that the incompatibility of quartz and nepheline resulting in the formation of albite + quartz restricts the field of analcime. A subsidiary effect may be that analcime is commonly reported (Winchell 1951, p. 333) to contain excess silica in solution. If this is the case the analcime formed by Fyfe is sure to contain more silica than that formed in a silica-free environment, and this could affect the stability field. Fyfe does not report the cell parameters of his synthetic analcimes. In three experiments performed by the authors in which analcime was formed in the presence of excess silica, significantly different cell parameters (see Figure 2) from those synthesized in a silica-free environment were obtained.

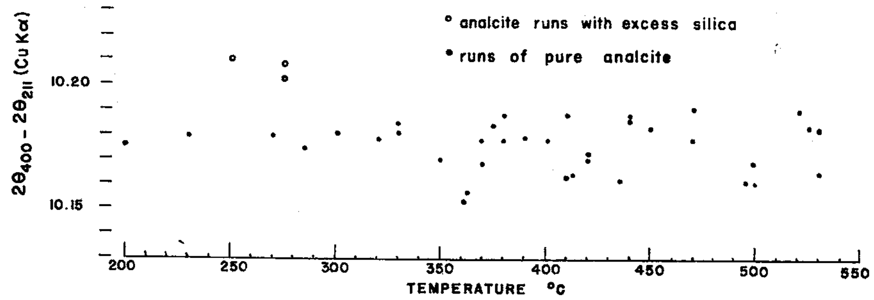

FIG. 2. Values of $2\theta_{400}$–$2\theta_{211}$ (Cu$K\alpha$) for analcime synthesized at different temperatures at a pressure of 15,000 p.s.i.

EXPERIMENTAL METHODS

1. Description of Apparatus

The essential components of the experimental apparatus consisted of an airdriven pump unit to supply the water pressure to the pressure vessels or "bombs" containing the charges, and a temperature-controlled furnace fitted around the bombs. The pump used was supplied by the Sprague Engineering Corporation of Gardena, California, model number S-216C-300. This pump, using laboratory air pressure of 90 p.s.i., will give a water pressure of up to 30,000 p.s.i. Tuttle (1949) cold-seal pressure vessels were used, and were supplied by Tem-Pres Incorporated, State College, Pennsylvania. The furnaces had a maximum permitted temperature limit of about 1100°C, and were supplied by the Fisher Scientific Company. The furnaces were controlled by Bristol Pyrometer Controllers, model number 478L. The controllers were calibrated against an accurate potentiometer circuit. This improved the controllers' accuracy to about ±10°C.

2. Sample Preparation

The formation of a dry mixture of the composition $NaAlSi_2O_6$ was accomplished by mixing α-Cristobalite, γ-Al_2O_3 and Na_2SiO_3 together in the correct proportions. α-Cristobalite and γ-alumina were used because they are relatively reactive forms of silica and alumina. The α-cristobalite was prepared by heating pure silicic acid (Mallinckrodt Chemical Works control number 75908) in an electric combustion furnace at 1520°C for 3½ hours. The γ-Al_2O_3 was prepared by heating $AlCl_3.6H_2O$ (Fisher Scientific Company, lot number 772760) in a fume cupboard for 2½ hours at red heat to drive off the chlorine, and then heating the resulting product in an electric muffle furnace at 900°C for 3¾ hours. The Na_2SiO_3 was prepared from $Na_2SiO_3.9H_2O$ (Fisher Scientific Company, lot number 763845). Because this latter compound is deliquescent, accurate weighing of portions was difficult. In order to overcome this difficulty the water was evaporated off in a drying oven and the compound weighed out as Na_2SiO_3. Each of the prepared chemical components was checked by x-ray diffraction methods to make sure that the required compounds had been prepared.

After the powders had been weighed out in the correct proportions to form $NaAlSi_2O_6$, they were ground for thirty minutes in an agate mortar, then placed in an hour-glass mixer, and passed through the screen two hundred times. It is believed that the powder became homogeneous through this process. The grain diameters of the resulting powder were almost uniform and averaged .0005 inches.

Sufficient of the prepared mixtures, to permit an x-ray investigation, were then placed in gold cylinders, and distilled water added. The cylinders were sealed by a welding method described by Yoder (personal communication). The sealed cylinders were placed in the bombs and a pressure of usually 15,000 p.s.i. applied. The charges were held at different temperatures between 200°C and 540°C. The temperature of 540°C is close to the upper limit of stability of analcime at this pressure while the temperature of 200°C is close to the lower limit at which the reactions will go readily. At the end of a run the bombs and charges were quenched in water, after which the pressure was released through a valve. The collapsed cylinders were removed and opened, and their contents analyzed by a Norelco high-angle goniometer.

3. X-ray Determination of Lattice Parameters

In order to determine the lattice parameters and phases present in the charges, they were examined with a Norelco high-angle diffractometer. Each charge was first ground with benzene to the same grain size. The diffractometer was set to oscillate between $2\theta = 14.5°$ and $2\theta = 26°$, because this interval contains the analcime peaks 400 and 211. At least six traverses were run over this interval and the distance between the peaks measured on a Norelco film-measuring device. The angles $2\theta_{400}$–$2\theta_{211}$ were thus measured directly on the six patterns, averaged, and then plotted against temperature upon a graph (see Figure 2, and

Table 1). The diffractometer settings used were: scanning rate, $\frac{1}{4}^\circ$ 2θ per minute; chart speed, $\frac{1}{8}$ inch per minute; rate meter scale factor, 4; multiplier, 1; and time constant, 4. Copper ($K\alpha$) radiation with nickel filter was used in every case. This method has an accuracy of about ±.01° 2θ. The errors in making this type of measurement have been rigorously discussed by Chayes & Mackenzie (1957).

TABLE 1.

RUNS MADE WITH A COMPOSITION OF ANALCIME + WATER

Run No.	Pressure (p.s.i.)	Temperature (C.)	Duration (hours)	$2\theta_{400}$–$2\theta_{211}$ (degrees)
4	15,000	380	170	10.189
6	15,000	435	92	10.162
9	15,000	400	95	10.179
12	15,000	410	95	10.163
13	15,000	420	95	10.170
17	20,000	380	96	10.178
19	15,000	390	90	10.179
20	15,000	525	12	10.184
23	15,000	375	95	10.184
26	15,000	500	54	10.161
37	15,000	300	48	10.181
38	15,000	350	48	10.170
39	15,000	412	48	10.164
40	15,000	450	48	10.184
41	15,000	500	48	10.169
43	15,000	320	48	10.179
44	15,000	370	90	10.179
46	15,000	470	90	10.192
47	15,000	520	90	10.191
48	15,000	270	90	10.180
49	15,000	285	96	10.175
50	15,000	330	96	10.181
51	15,000	362	96	10.157
52	15,000	360	96	10.153
53	15,000	370	96	10.169
55	15,000	440	192	10.189
56	15,000	470	192	10.178
57	15,000	530	192	10.165
60	15,000	530	192	10.183
61	15,000	440	96	10.187
62	15,000	330	96	10.185
63	15,000	495	96	10.162
64	15,000	410	96	10.188
65	15,000	420	96	10.173
67	15,000	230	96	10.180
68	15,000	200	96	10.176

RUNS WITH SILICA IN EXCESS OF THE STOICHIOMETRIC AMOUNT NECESSARY FOR THE FORMATION OF ANALCIME

Run No.	Pressure (p.s.i.)	Temperature (C.)	Duration (hours)	$2\theta_{400}$–$2\theta_{211}$ (degrees)
73	15,000	250	24	10.207
74	15,000	275	24	10.210
75	15,000	275	24	10.203

EXPERIMENTAL WORK

The runs were all carried out within the stability field of analcime determined by Yoder. Most of the runs were at 15,000 p.s.i., and of two to eight days' duration. Approximately eighty runs were made, half of which were discarded as unreliable or useless because of leakage or failure of pressure or temperature controlling devices, etc. The results of the remaining thirty-nine runs, with the conditions for each in which analcime was synthesized, are listed in Table 1. Figure 2 is a plot of temperature against $2\theta_{400}-2\theta_{211}$.

INTERPRETATION OF RESULTS

It is evident from Figure 2 that there is a scatter in the results obtained from $2\theta_{400}-2\theta_{211}$ and it is pertinent therefore to enumerate some of the factors affecting the accuracy of this measurement. These factors in general have been discussed by Mackenzie (1957).

The major factors which may cause a variance in $2\theta_{400}-2\theta_{211}$ are: (1) variations in the starting compositions; (2) differences in the initial grain size of the charges; (3) duration of the run; (4) variation in water pressure; (5) errors in the diffractometer together with differences in sample preparation and mounting; (6) the possibility of O^{-2} ions being replaces by OH^- ions and the possibility of excess water in the analcime structure; (7) different degrees of ordering of the ions, chiefly the Al and Si ions.

(1) The composition was carefully controlled and was constant with the exception of runs 73, 74 and 75 in which excess silica was present. The parameters of analcimes synthesized in these runs were significantly different from the average of the other runs, presumably due to the analcime structure taking some silica into solid solution.

(2) Mackenzie (1957), in a study of the effect of variation in grain size of the starting material on the lattice parameters of synthetic albite, found that a variation of 0.0022 inches in grain diameter caused a corresponding variation of $0.008°2\theta$ in the angle $2\theta_{131}-2\theta_{1\bar{3}1}$ Cu$K\alpha$). The variation in grain diameters in the starting materials in this study was 0.0014 inches and therefore errors due to this kind of variation are probably small, perhaps of the same order as that for albite.

(3) The duration of the runs was varied at certain temperatures, without significantly affecting the parameter $2\theta_{400}-2\theta_{211}$. It was, therefore, assumed that equilibrium had been reached. Even if equilibrium has not been established any variation in cell parameters as a function of temperature would probably be evident.

(4) All the runs were at 15,000 p.s.i. except one at 20,000 p.s.i., and thus the pressure was not a variable in most of these experiments. There was

no significant difference between the run at 20,000 p.s.i. (run no. 17) and runs at 15,000 p.s.i. at a similar temperature (runs 44, 23, etc.).

(5) The diffractometer was checked several times using a silicon standard and satisfactory accuracy was obtained. As mentioned previously, the errors involved in the measurement of the angle between two peaks have been discussed by Chayes & Mackenzie (1957). In the present work the error is of the order of $\pm.010°2\theta$ for 95% probability.

(6) Smith & Tuttle (1957) suggested that replacement of O^{-2} ions by OH^- ions might affect the lattice parameters of nepheline. This suggestion is not as yet proved. Winchell (1951, p. 333) reports that analcime often contains excess H_2O. It seems likely then that analcime synthesized in the present experiments contains variable amounts of water. Some of this water will undoubtedly be lost on exposure to the air. The effect of variable amounts of water on the lattice parameters is likely to be small compared with a change in the Si–Al–O framework.

(7) A change in ordering at the Al–Si sites in analcime was encouraged by synthesizing the mineral at different temperatures. It has been suggested by Mackenzie (1957) that a change in ordering of Al and Si in albite can be detected by measurement of cell parameters. It can be seen from Figure 2, and the preceding discussion that the scatter of points is of the order of the expected experimental errors, chiefly those under sections (2) and (5) with possibly some variation due to (6). Thus there does not appear to be a uniform change which can be ascribed to a change in the ordering of analcime in a uniform manner with different temperature of formation. This is rather surprising in view of the proposed structure of Taylor. It may suggest that analcime has in fact an ordered or nearly ordered structure or alternatively that one cannot detect the disordering of the Si–Al ions by measurement of cell parameters.

Correlation with Natural Analcimes

It would be desirable to compare the *x*-ray patterns of natural analcimes with the synthetic varieties. In order that this may be done accurately it is necessary, of course, to have pure natural analcimes, which have been chemically analyzed. There were no chemically analyzed pure specimens available to the authors, indeed, they are probably nonexistent and furthermore there are no optical methods which permit the determination of composition by measurement of refractive indices. Analcime is often reported to contain excess SiO_2, H_2O, Al_2O_3, CaO or K_2O. It has been suggested by Fyfe (1958, p. 168) that there is possibly a solid solution between analcime and its calcium analogue. The latter mineral has been synthesized by Fyfe and a natural occurrence of a

Ca-analcime, wairakite has been reported (Steiner 1953). In addition Winchell (1951, p. 253) reports that there is a series, rather surprisingly, between pollucite ($CsSiAl_2O_6$) and analcime despite the fact that pollucite reportedly contains no zeolitic water. In view of these complications, until more is known about the compositional variations of natural analcimes, no meaningful comparisons with synthetic varieties can be made here.

A few natural specimens were *x*-rayed by the authors and appeared to have somewhat smaller values of $2\theta_{400}$–$2\theta_{211}$ than the synthetic materials.

CONCLUSIONS

Within the limit of experimental error there is no change in the cell parameter $2\theta_{400}$–$2\theta_{211}$ of analcimes synthesized within the temperature range 200°C. to 540°C. and at a pressure of 15,000 p.s.i. This seems to indicate that there is no change in the degree of ordering of the Al–Si sites in analcime with different temperatures of formation. This is perhaps somewhat surprising in view of the presumed structure.

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