THE SYSTEM NaAlSiO₄ (NEPHELINE)-NaAlSì₃O₈
(ALBITE)-H₂O*

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ABSTRACT

The system NaAlSiO₄-NaAlSì₃O₈-H₂O has been investigated in the temperature range 200°-700° C. at pressures of 5000 to 45,000 psi. The following minerals and compounds were synthesized and their stability investigated: nepheline solid solutions, albite, analcite solid solutions, nepheline hydrate I, paragonite, zeolite “B” and species "Y". Natrolite was found to be unstable in the presence of excess water vapor under the pressure and temperature conditions utilized. Experimental investigations and theoretical calculations indicated that the alkali-rich portion of the system does not remain ternary at low temperatures under the conditions of the experiments.

The following transitions, within the P-T-X region involved, were studied in detail:
(1) nepheline hydrate = nepheline + water.
(2) analcite solid solution = nepheline solid solution + albite + water.
(3) analcite solid solution (comp. = NaAlSiO₄·1.5H₂O) = albite + water.

Analcite was found to exhibit solid solution through an extensive range of composition, but field and laboratory evidence suggests that part of it may be metastable. The range of solid solution found in nature is more restricted than the range determined experimentally.

Petrogenetic implications of the investigation are discussed. Preferential solubility of soda and alumina in the vapor in runs made with glasses whose compositions lie in the alkali-rich portion of the system, indicates a possible mode of nephelinization of country rocks surrounding bodies of alkaline rocks. Experimental work carried out on the formation of the assemblages analcite solid solution + nepheline solid solution and analcite solid solution + albite may be useful in ascertaining the temperature and pressure of development of these assemblages in nature. The origin of analcite in deeply buried slightly metamorphosed rocks derived from pyroclastic materials is discussed.

INTRODUCTION

Experimental determinations of the stability of minerals have been useful in laying down the basic principles necessary for the interpretation of petrological features associated with igneous activity. In the late stages of igneous activity and in metamorphism and weathering, where water plays a very important role, experimental determination of the stability of hydrous minerals and the stability of anhydrous minerals in the presence of water becomes important. Phase-equilibrium relations in the system NaAlSiO₄-NaAlSì₃O₈-H₂O, both stable and metastable, have been investigated and will be described in this paper. An attempt will be made to interpret the petrological significance of minerals occurring in this system.

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The following ternary compounds are found in the system NaAlSiO₄-NaAlSi₃O₈-H₂O: nepheline (NaAlSiO₄), albite (NaAlSi₃O₈) and jadeite (NaAlSi₂O₆), all of which occur as minerals in nature. All of these minerals have been synthesized by different workers in different laboratories. The following quaternary compounds have been reported in this system: analcrite (NaAlSi₂O₆·H₂O), natrolite (Na₂Al₂Si₃O₁₀·2H₂O), nepheline hydrate I (NaAlSiO₄·½H₂O), nepheline hydrate II (NaAlSiO₄·H₂O), zeolite “A” (NaAlSiO₄·2.35H₂O), and zeolite “B”. Among these, analcrite and natrolite occur as minerals in nature. Analcite forms readily in hydrothermal runs, but natrolite has only recently been synthesized (Hoss and Roy, 1959). Hydronephelite has been reported to occur as an alteration product of nepheline (Thugutt, 1892; Tilley and Harwood, 1931; Dunham, 1933). Barrer and White (1952) suggested that it may be the same as nepheline hydrate I. Nepheline hydrate II, zeolite “A” and zeolite “B” have been synthesized by different workers, but have not yet been reported from nature.

Greig and Barth (1938) investigated liquidus relations in the system NaAlSiO₄-NaAlSi₃O₈, and the extent of solid solution of albite in nepheline and vice versa. They found that nepheline is relatively insoluble in albite, but takes up a large amount of albite in solid solution (33% by wt.). They found the eutectic temperature to be at 1068° ± 5° C. at a composition Ab₇₆Ne₂₄ (by wt.). Their conclusions in regard to the extent of solid solution were tentative, because they suspected that the glasses did not crystallize completely. MacKenzie (1954), while working in the system NaAlSiO₄-NaAlSi₃O₈-H₂O at 1000 bars, found the minimum melting temperature to be at 870° ± 5° C. at the composition Ab₇₂Ne₂₈ (by wt.). He also found the limit of nepheline solid solution to be about Ne₅₃Ab₄₇ (by wt.) at 750° C.

Jadeite was first synthesized by Coes (1953), by the reaction between sodium sulfate, kaolin and silica at a pressure of 20,000 kgm/cm², at 900° C. Later, several other workers were able to synthesize jadeite and determine its stability (Robertson, Birch and MacDonald, 1957; Griggs, Kennedy and Fyfe in Fyfe, Turner and Verhoogen, 1958, p. 175). Yoder studied the system NaAlSiO₄·H₂O in an attempt to synthesize analcrite and jadeite and determine their fields of stability (Yoder, 1950, 1954). Sand, Roy and Osborn (1957) studied the stability of minerals in the quaternary system Na₂O·Al₂O₃·SiO₂·H₂O. They were able to synthesize analcrite from gels of albite composition at low temperatures, but according to them, “...this converted gradually to albite at temperatures above 290° C. indicating that the latter is the stable phase.” Fyfe, Turner and Verhoogen (1958) determined part of the boundary for the reaction analcrite+quartz=albite+quartz+water. They worked with
oxide mixes of composition NaAlSi$_4$O$_{10}$ in the presence of water vapor. Coombs et al. (1959) also studied the same reaction with oxide mixes (NaAlSi$_3$O$_8$+SiO$_2$) and with NaAlSi$_3$O$_8$ glass.

Barrer and White (1952) heated gels ranging in composition from Na$_2$O·Al$_2$O$_3$·2SiO$_2$ to Na$_2$O·Al$_2$O$_3$·10SiO$_2$ at different temperatures and atmospheric pressure, frequently in the presence of excess NaOH solution. In the range Na$_2$O·Al$_2$O$_3$·2–6SiO$_2$, they were able to synthesize the following minerals and compounds: nepheline, nepheline hydrate I, nepheline hydrate II, analcrite, albite, paragonite, compound L (2Na$_2$O·Al$_2$O$_3$·6SiO$_2$·2H$_2$O), “basic” sodalite, “basic” nosean, “basic” cancrinite and compound N. Nepheline hydrate I and nepheline hydrate II could be synthesized from gels of NaAlSi$_4$O$_4$ composition, and they gave the following compositions for these two compounds: Na$_2$O·Al$_2$O$_3$·2SiO$_2$·2H$_2$O for nepheline hydrate I and Na$_2$O·Al$_2$O$_3$·2SiO$_2$·2H$_2$O for nepheline hydrate II. Paragonite was also synthesized from NaAlSi$_4$O$_4$ gel. Analcite was synthesized from gels of a wide range of composition (Na$_2$O·Al$_2$O$_3$·3–10SiO$_2$). From gels of NaAlSi$_3$O$_8$ composition, analcrite was synthesized below 300° C., a mixture of analcrite and albite in the range 300°–420° C., and only albite above 450° C. This work cannot be considered as phase-equilibrium investigations in the system NaAlSi$_4$O$_4$–NaAlSi$_3$O$_8$·H$_2$O as they often used excess NaOH solution for the synthesis of the minerals and compounds. Thus for example, nepheline hydrate II, compound L, compound N, etc., were synthesized only in the presence of excess NaOH. MacKenzie (1957), while investigating the transformation high albite→low albite, reported the presence of some analcrite at 400° C. and only analcrite at 300° C. in runs made with glass of NaAlSi$_3$O$_8$ composition in the presence of water. Guyer, Ineichen and Guyer (1957) synthesized analcites from compositions within the range Na$_2$O·Al$_2$O$_3$·2–10SiO$_2$ in order to study their sorbing properties. Some sodalite was present together with analcite in the products of crystallization of NaAlSi$_4$O$_4$ gel. Breck et al. (1956) were able to synthesize two zeolitic compounds, zeolite “A” and zeolite “B”, from NaAlSiO$_4$ gel in the presence of water.

**Techniques**

Investigations in the system NaAlSi$_4$O$_4$–NaAlSi$_3$O$_8$·H$_2$O were carried out using gels and glasses.

Gels were prepared by a method described by Roy (1956). Some other gels were prepared by mixing together Ludox* silica sols, standardized aluminum nitrate and sodium hydroxide solutions and evaporating to

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* duPont Co. trade name.
dryness. Only rarely were the gels used as such; in most cases they were melted at high temperatures to give homogeneous glasses. Glasses varying from Na₂O·Al₂O₃·SiO₂ to Na₂O·Al₂O₃·6SiO₂, were made by these methods.

NaAlSiO₄ and NaAlSi₃O₈ glasses were also prepared by the method described by Schairer and Bowen (1956). Glasses intermediate in composition were prepared by repeated fusion and grinding of these two end members. The composition and refractive index of the glasses prepared by this method are listed in Table I.

### Table I. Refractive Indices of Glasses

<table>
<thead>
<tr>
<th>Composition of Glasses (Mol. Ratio)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O : Al₂O₃ : SiO₂</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1 : 1 : 2.00</td>
</tr>
<tr>
<td>2</td>
<td>1 : 1 : 2.25</td>
</tr>
<tr>
<td>3</td>
<td>1 : 1 : 2.50</td>
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<td>4</td>
<td>1 : 1 : 2.75</td>
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<td>5</td>
<td>1 : 1 : 3.00</td>
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<td>1 : 1 : 3.50</td>
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<td>1 : 1 : 4.00</td>
</tr>
<tr>
<td>11</td>
<td>1 : 1 : 6.00</td>
</tr>
</tbody>
</table>

The runs were made in cold-seal pressure vessels described by Tuttle (1949). Approximately 20 mg. of the charges were sealed in small gold tubes with about 20 mg. of water. Care was taken to add excess water, since the scope of the investigation did not extend to the water-deficient region. The runs were considered to be good only when the samples appeared to be wet on opening the tubes after the runs. External hydrothermal pressure was applied to the sealed tubes by means of a Sprague Electric Company air-operated pump and a system of valves. The temperature was controlled by a Brown Electronic Controller. The products of the runs were examined by standard microscopic and x-ray powder diffraction procedures.

**Phases Synthesized**

Runs were made in the systems NaAlSiO₄·H₂O, NaAlSi₃O₈·H₂O, Na₂Al₂Si₅O₁₆·H₂O and NaAlSiO₄·NaAlSi₃O₈·H₂O (Saha, 1959b). Attempts were also made to determine the stability of the different phases by the decomposition of synthetically prepared and natural crystalline
phases. The following phases have been synthesized: nepheline, nepheline hydrate I, paragonite, zeolite “B,” analcite, albite and species “Y.” X-ray powder diffraction patterns of all the phases synthesized, except for albite, are shown in Fig. 1. Brief descriptions of the phases will be given here.

**Nepheline:** The nepheline crystals synthesized from glass of NaAlSiO₄ composition were apparently identical with the low-temperature form of nepheline described by Smith and Tuttle (1957). They appeared as hexagonal basal plates and prismatic laths. The maximum grain-size recorded was 0.18 mm × 0.04 mm. Nepheline synthesized from glasses richer in silica than NaAlSiO₄ had a somewhat different habit; the crystals occurred as short square prisms and hexagonal basal plates full of vapor inclusions.

**Nepheline Hydrate I:** Nepheline hydrate I (the convention adopted by Barrer and White (1952) has been retained here) appeared as small irregular grains, never more than 35 microns in diameter and rarely with crystalline outlines. The crystals were determined to be biaxial, and the refractive indices were \( \alpha = 1.499 \pm 0.002 \), \( \gamma = 1.503 \pm 0.002 \). The values are somewhat lower than the values given by Barrer and White (\( \alpha = 1.503, \beta = 1.506, \gamma = 1.508 \)).

**Albite:** Albite occurred as well crystallized euhedral grains when prepared from compositions near the silica-deficient boundary of the solvus (Na₂O·Al₂O₃·3SiO₂), but became blocky and full of inclusions in preparations having compositions on the albite side of the solvus boundary (Na₂O·Al₂O₃·4-6SiO₂). Fine clusters of needles and plates of albite formed readily in runs made with Na₂O·Al₂O₃·4-6SiO₂ glasses at high temperatures. The maximum dimensions of the albite laths synthesized in this range were: 0.04 mm. in length and 0.014 mm. in width. From x-ray powder diffraction patterns, they were found to be identical with the high-temperature modification of albite synthesized by Bowen and Tuttle (1950).

**Analcite:** Analcite was synthesized from glasses of compositions within the range Na₂O·Al₂O₃·2-3SiO₂. In very long runs (21 days—90 days) at low temperatures (200°C), made with glass of NaAlSiO₄ composition as starting material, analcite began to appear as round isotropic grains, replacing zeolite “B.” Microscopically the grains were too small and too intimately mixed with zeolite “B” to make refractive-index determinations; but the characteristic reflections of analcite were present in the x-ray powder diffraction patterns. Analcite prepared from Na₂O·Al₂O₃·2.25-5SiO₂ glasses had similar habit of growth, the size of the individual crystals attaining a maximum diameter of 0.09 mm. in products of runs made with Na₂O·Al₂O₃·3SiO₂ glass. Analcite formed very readily from glass of NaAlSiO₄ composition in runs made below 400°C. The crystals had a maximum diameter of 0.04 mm. Complete crystallization of the glass to a fine-grained aggregate of analcite crystals (except for \( \approx 1\% \) paragonite) indicates that the analcite has the composition NaAlSiO₄ together with zeolitic water (Saha, 1959a).

The synthetic crystals were isotropic, and the refractive index changes considerably with SiO₂ content as shown in Table II.

It was not possible to measure the refractive index of analcite synthesized from glasses within the range of composition Na₂O·Al₂O₃·2-3SiO₂ because of the presence of paragonite flakes, which surround the analcite grains.

The author would like to correct an error in a previous paper (Saha, 1959a) concerning the x-ray investigation of analcite. Inadvertently, tables for CuKα radiation were used for calculating the lattice parameter of analcite of different compositions, instead of tables for CuKα radiation. Table III shows the displacement of (639) peak for analcite of different compositions, both synthetic and natural, and in this the lattice parameters have been calculated correctly. Fig. 2 shows the displacement of the (639) peak. Some new data have
also been incorporated, on the basis of which a break in the curve for the displacement of (639) peak of analcite, approximately at the composition \( \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.75\text{SiO}_2 \), can be postulated. This break represents the limit of solid solution of analcite for the alkali-rich portion of the system.

*Species “Y”:* At very low temperatures (200° C.) in comparatively short runs (2–8 days)
### Table II. Refractive Indices of Analcite

<table>
<thead>
<tr>
<th>Composition of Glasses (Mol. Ratio)</th>
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</tr>
</thead>
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<tr>
<td></td>
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<tr>
<td>Na₂O : Al₂O₃ : SiO₂</td>
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<tr>
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### Table III. Displacement of (639) Peak of Analcites of Different Compositions

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<th>No.</th>
<th>Composition</th>
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<th>a₀ (Å)</th>
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<td>(CuKα₁ radiation)</td>
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<td>Synthentic analcites:</td>
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<td>16</td>
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Natural Specimens:

<table>
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<th>No.</th>
<th>Composition</th>
<th>2θₓₐn(639)−2θₙE(381)</th>
<th>a₀ (Å)</th>
</tr>
</thead>
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<td></td>
<td></td>
<td>(CuKα₁ radiation)</td>
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<tr>
<td>17</td>
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<td>1 : 1 : 5.45 : 2.70²</td>
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</tr>
<tr>
<td>19</td>
<td>Natrolite converted to analcite¹</td>
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<td>1.575</td>
</tr>
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</table>

¹ Composition of glasses used as starting material.
² Two specimens of analcite from Yavapai County, Arizona; compositions assumed to be average of two analyses given by Ross (1928).
³ Natural natrolite from Habsena, Bohemia, Specimen No. 453.6, Genth collection.
⁴ α₁ and α₂ peaks of d(639) not well resolved. Cannot be measured accurately.
made with glasses of compositions in the range $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2-3\text{SiO}_2$, a mixture of two phases appeared, which were too fine-grained to be identified optically. Certain lines appearing in the powder diffraction spectrometer charts (Fig. 1) have been assigned to zeolite "B," and the other lines have been assigned to species "Y." In longer runs (21 days), the lines for species "Y" disappeared, the intensities of the lines for zeolite "B" decreased, and analcite started to appear, indicating that both zeolite "B" and species "Y" are metastable phases. Glasses of composition $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ crystallized directly to zeolite "B" in short runs (8 days), which was replaced by analcite in longer runs (21-90 days). It is possible that species "Y" is a mixture of more than one phase.

Zeolite "B": Zeolite "B" was synthesized from glasses within the range $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2-6\text{SiO}_2$ at low temperature (200°C) in short runs (1½-21 days). Crystallization was best in runs made with $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ glass, but some glass remained in short runs made with glasses of $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3-4\text{SiO}_2$ compositions. $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ glass did not crystallize appreciably in runs of short duration. Some zeolite "B" appeared in longer (21 days) runs. Still longer runs (90 days) proved that zeolite "B" is definitely metastable with respect to analcite, as it is totally ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3-4$ glasses) or partially ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ and $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ glasses) replaced by it. The compound appeared to be weakly birefringent, and the average refractive index decreased toward the silica-rich end as shown in Table IV.

This suggests that there is a solid-solution relationship. However, the $x$-ray powder diffraction spectrometer of zeolite "B" synthesized from glasses of different compositions did not indicate any appreciable displacement of the peaks. The cell dimension for the pseudo-cubic unit cell was measured, and found to be $10.05 \pm 0.05 \text{ Å}$. 

Paragonite: Small platy grains of paragonite, 22-7 microns in length and 7-1 microns in

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**Fig. 2.** Variation of $d_{(639)}$ spacing of synthetic analcites with variation of $\text{SiO}_2$ content.
diameter, appeared in intimate association with nepheline hydrate I at the stability range of the latter. They could be very easily distinguished from nepheline hydrate I by their much higher refractive indices, but it was impossible to identify them by the X-ray diffraction spectrometer alone, because of the small quantity available. Weak, diffuse reflections were obtained at 2θ = 9° (CuKα), corresponding to the basal plane of paragonite, and 2θ = 20° (CuKα), which also corresponds to another strong paragonite peak (Barrer and White, 1952). Two other peaks could be observed in an electron diffraction photograph which also correspond to paragonite (Fig. 1).

Paragonite also appeared quite frequently in association with analcite in runs made with glasses of compositions within the range Na2O·Al2O3·2-3SiO2, but the amount decreased quite considerably in runs made with glasses higher in silica than Na2O·Al2O3·3SiO2. This phase was mentioned as an “unidentified phase” in a previous paper by the author (Saha, 1959a). The mineral occurred as very fine flakes forming clusters around analcite grains.

**Phase-Equilibrium Studies in the System NaAlSiO4-H2O**

Figure 3 has been drawn using the data obtained (Saha, 1959b, Table II). The crystalline phases, stable and metastable, obtained in the products of the runs, have been marked with different symbols. The curve for the transition: nepheline hydrate I + water = nepheline + water has been drawn as a solid line. Nepheline hydrate I crystallized readily below the curve from runs made with glass of NaAlSiO4 composition. At 15,000 psi and 445° ± 10° C., nepheline hydrate I decomposes to yield nepheline and vapor; Sand, Roy and Osborn (1957) found the transition temperature to be 460° C. at this pressure.

Efforts made to synthesize nepheline hydrate I by the reaction of nepheline crystals with water below the curve resulted only in the appearance of analcite. On the other hand, even in very long runs (3 months) made with glass and with nepheline hydrate I crystals, only nepheline hydrate I crystals could be detected. It was therefore impossible to establish the stability of nepheline hydrate I.

In runs made in the lower stability range of nepheline hydrate I, platy grains of a phase identified as paragonite appeared. Barrer and White (1952) also reported the synthesis of paragonite from gels of NaAlSiO4 composition.

**Table IV**

<table>
<thead>
<tr>
<th>Composition of Glasses (Mol. Ratio)</th>
<th>Average Refractive Index of Zeolite “B”</th>
</tr>
</thead>
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<td>Na2O : Al2O3 : SiO2</td>
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<tr>
<td>1</td>
<td>1.501 ± 0.002</td>
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<tr>
<td>2</td>
<td>1.493 ± 0.002</td>
</tr>
<tr>
<td>3</td>
<td>1.485 ± 0.002</td>
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</table>
Barrer and White (1952, Fig. 1-f), while working with gels of NaAlSiO₄ composition, were able to synthesize another hydrated phase, which they designated as nepheline hydrate II (Na₂O·Al₂O₃·2SiO₂·½H₂O), just above the stability field of nepheline hydrate I. They were able to synthesize this phase only in the presence of excess NaOH solution, and nepheline always appeared with this phase (1952, Table I). Subsequent investigators (Sand, Roy and Osborn, 1957) failed to synthesize this phase. Attempts were made to synthesize this phase during this investigation, but without success.

A compound of the composition Na₂O·Al₂O₃·2SiO₂·4.5H₂O designated by Breck et al. (1956) as zeolite “A” was reported to have been synthesized in very short runs (approximately 3 hours, personal communication with Dr. Breck). Since the minimum duration of any runs made during the present investigation was one day, zeolite “A” was not synthesized. Zeolite “A” is replaced by zeolite “B” in longer runs (Breck, personal communication). This suggests that zeolite “A” is a metastable phase under this condition.

Species “Y” and zeolite “B” are metastable phases which were partly

![Fig. 3. The system NaAlSiO₄·H₂O](image-url)
replaced by analcite in relatively longer runs (21 days—3 months). Analcite was very imperfectly crystallized in these runs, and it was not possible to determine the composition of analcite by the method of measuring the position of (639) peak, as described in a previous paper (Saha, 1959a). It seems possible that analcite is the stable phase at low temperatures crystallizing from a glass of NaAlSiO₄ composition. The presence of the metastable phases made it impossible to determine the transition curve: analcite solid solution + H₂O = nepheline hydrate I + H₂O, if such a curve exists. A great deal of additional work must be done before this curve can be located accurately.

Thus experimental investigations suggest that nepheline is not stable below 400°-500° C. at moderate to high pressures in the presence of excess water. Glasses of nepheline composition, heated within the range 265°-450° C. and at various pressures, crystallize directly to nepheline hydrate I and some paragonite, the latter possibly due to some loss of soda and alumina and probably silica in the vapor. Also nepheline crystals are directly converted to analcite when heated at 300°-395° C. and 30,000-45,000 psi. These facts have an important bearing on the petrogenesis of alkaline rocks, which are known to be markedly rich in volatiles (Shand, 1947). It is expected that nepheline hydrate I or analcite would be abundant as alteration products, where there has been sufficient time for the magma to cool down slowly and yet retain a considerable amount of water under high pressure in the fissures. It is also expected that analcite rather than nepheline hydrate I will be abundant as a replacement product in volcanic rocks, rich in alkalies and glass, and where there is a chance for the alkali- and alumina-rich vapor phase to escape.

Reports on the occurrence of any natural counterpart of nepheline hydrate I are rare. As Barrer and White state, “hydronephelite” reported by Thugutt (1892) may well be nepheline hydrate I, but he did not give any identifying physical data. Walker and Parsons (1926) have described the presence of a zone (½-1") of white to pink porcelaneous hydronephelite surrounding cancrinite in the nepheline syenite area of French River, Ontario. But the analysis of the mineral, even after deducting 11.19% calcite, contains too much alumina (28.88%) to be called hydronephelite. Tilley and Harwood (1931) have described the alteration of nepheline to fibrous masses of hydronephelite in titanargite rocks. The mineral is uniaxial, elongation positive and the refractive indices (\(\omega = 1.490, \epsilon = 1.500\)) can be compared to those of synthetic nepheline hydrate I (\(\alpha = 1.499, \gamma = 1.503\)). Dunham (1933) also reported the occurrence of “hydronephelite” in undersaturated rocks from Hawaii. Jeremie (1948) has described the occurrence of “hydronephelite” derived from nepheline in association with aegirine-augite, apatite, sphene, soda
amphibole and biotite in a rock which has been named mestigmerite by Lacroix. No x-ray data for natural “hydronephelite” have been published.

The rare occurrence of nepheline hydrate I in nature is in contrast to the observation that it can be grown readily from glass or gel of nepheline composition in the laboratory. A possible explanation of this can be offered only when the crystallization behavior of glasses of other compositions in the system NaAlSiO$_4$-NaAlSi$_3$O$_8$-H$_2$O are considered. The data obtained (Saha, 1959b, Tables II, VIII and IX) show that nepheline hydrate I can be crystallized from glass of NaAlSiO$_4$ composition only. A little excess silica completely inhibits its growth, and since normal alkaline rocks contain more silica than end-member nepheline, this can explain why nepheline hydrate I is such a rare mineral. Also the possibility that nepheline hydrate I appears as a metastable phase in the hydrothermal runs cannot be excluded.

On the other hand, analcite has quite often been reported from undersaturated rocks, sometimes in close association with nepheline, and hydrothermal treatment of synthetic nepheline at low temperatures always yielded a mixture of nepheline and analcite. An explanation of this peculiar behavior, i.e., loss of soda and alumina, will be discussed in more detail later. At low temperatures, it is possible that structural control plays an important part in the crystallization of multi-component glasses and gels. It is very difficult and in some cases impossible to determine the stability of different phases at these low temperatures. Moreover, volatile associated with alkaline rocks contain not only water vapor, but also other compounds bearing Cl$^-$, F$^-$, SO$_4^{2-}$, etc., and it is quite likely that the presence of minerals like cancrinite, sodalite, etc., will restrict the stability field of nepheline hydrate I. As a matter of fact, these minerals do form very readily in undersaturated plutonic and volcanic rocks.

**Phase-Equilibrium Studies in the System NaAlSi$_3$O$_8$-H$_2$O**

Figure 4 has been drawn on the basis of the hydrothermal runs.* Some complications arose when it was found that analcite is a phase which crystallized very rapidly from glass of NaAlSi$_3$O$_8$ composition in the presence of water vapor, and once formed, it was very difficult to decompose it below 450$^\circ$ C. Even in runs brought up to temperature and pressure in ten minutes, some analcite grains were always observed under the microscope, though characteristic analcite peaks were not observed in the x-ray diffraction spectrometer chart. The runs near the transition temperatures were not conclusive because of the presence of both the phases

* The complete data are given in Saha, 1959b.
in the product. The dotted line has been drawn on the basis of the proportion of the two phases present, and it is quite possible that the transition curve may be raised or lowered by as much as 25°C.

Several long runs (3 months) were made to investigate the stability of analcite solid solution of NaAlSi$_3$O$_8$ composition. Very finely ground specimens of high-, low-, and authigenic albite were used to see whether they would change over to analcite of NaAlSi$_3$O$_8$ composition. Runs were made at 300°C and 30,000 psi, within the range of crystallization of analcite solid solution from NaAlSi$_3$O$_8$ glass. No change in the specimens was observed. On the other hand, only analcite crystallized from identical runs made with NaAlSi$_3$O$_8$ glass. Thus it cannot be said that analcite solid solution of NaAlSi$_3$O$_8$·1.5H$_2$O composition is the stable phase at these temperatures.

Fyfe, Turner and Verhoogen (1958) determined the position of the pressure-temperature curve for the reaction analcite+quartz=albite+quartz+water (1). Their transition curve appears to be somewhat lower (≈50°C) than the curve for the reaction analcite(ss)=albite+water (2) determined by the author (Fig. 4), even after allowing the rather uncertain nature of the curve for reaction (2). This can be explained readily because they were working with oxide mixes of composition NaAlSi$_4$O$_{10}$, richer in silica than the composition of albite (NaAlSi$_3$O$_8$). It is possible that the extent of analcite solid solution does extend beyond NaAlSi$_3$O$_8$ but not quite up to the composition NaAlSi$_4$O$_{10}$, and hence the transition

![Figure 4. The system NaAlSi$_3$O$_8$·H$_2$O.](image)
The appearance of analcite in runs made with glass of NaAlSi$_3$O$_8$ composition at low temperatures obviously has important geochemical significance in the petrogenesis of saturated igneous rocks, if the experimental results represent stable equilibrium. Analcite of NaAlSi$_3$O$_8$·1.5H$_2$O composition has not been reported from nature, but analcite intermediate in composition between NaAlSi$_2$O$_8$ and NaAlSi$_3$O$_8$ has been reported from sedimentary rocks (Ross, 1928, 1941). In one instance (Ross, 1941) the sedimentary series is composed almost exclusively of analcite together with a small proportion of glauconite and plagioclase. Keller (1952) also reported authigenic analcite intermediate in composition between NaAlSi$_3$O$_9$·H$_2$O and NaAlSi$_3$O$_8$·1.5H$_2$O from the Popo Agie member of the Chugwater formation. Extensive deposits of analcite also occur in the Green River formation of Utah, Colorado and Wyoming (Bradley, 1928) associated with other zeolites, but its chemical composition is not known. These occurrences suggest that natural analcite approaching NaAlSi$_3$O$_8$·1.5H$_2$O composition should be looked for in sedimentary rocks.

Transitions from zones rich in analcite to zones rich in albite in thick formations of slightly metamorphosed sedimentary rocks have been observed in some places (Coombs, 1954). The pressure probably does not play a very important role in the case $P_{\text{total}} = P_{H_2O}$, as is evident from the nature of the transition curve (Fig. 4, cf. Coombs et al., 1959, fig. 7), but the geothermal gradient associated with the increase in depth and pressure is very important. Investigation of environmental conditions of deposition and application of phase-equilibrium data on the transition: analcite (NaAlSi$_3$O$_6$·1.5H$_2$O) = albite + water may be helpful in defining a temperature within the assemblages of the recently proposed “zeolite facies.” The work of Coombs et al. (1959) on the reaction analcite + quartz = albite + quartz + water will be more helpful in the case of analcime + quartz assemblages described by Coombs (1954).

**Stability of Minerals and Compounds in the System NaAlSiO$_4$-NaAlSi$_3$O$_8$-H$_2$O**

Phase-equilibrium relationships in the system NaAlSiO$_4$-NaAlSi$_3$O$_8$-H$_2$O can be conveniently represented by means of a series of isobaric triangles, as indicated in Fig. 5. They are based on the runs made at 15,000 psi (Saha, 1959b). NaAlSi$_4$O$_4$, NaAlSi$_3$O$_8$ and H$_2$O constitute the three components; it has been assumed that the system is ternary. This holds
Fig. 5. Isobaric (15,000 psi.), isothermal sections for the system NaAlSiO₄-NaAlSi₃O₈-H₂O. Data plotted in mol.%. 

- Na Hy I: Nepheline Hydrate I
- An₉²: Analcite Solid Solution
- Na₂₅: Nepheline Solid Solution
- Ab: Albite
- L: Liquid
- V: Vapor
true in general, except, perhaps, for glasses within the range Na$_2$O·Al$_2$O$_3$·2–2.75SiO$_2$, at low temperatures (200°–400° C.). The limit of solid solution of analcite (Na$_2$O·Al$_2$O$_3$·2.75SiO$_2$) has been drawn on the basis of the curve for the shift in (639) peak position of analcite (Fig. 2).

**Nepheline Solid Solution**

The extent of solubility of albite in nepheline has been determined. It was found that at 600° C. and 15,000 psi, nepheline can take up to 33% by wt. of albite into solid solution. MacKenzie (1954) placed the solvus position at 25% by wt. of albite at 750° C. and 1000 bars water vapor pressure. The displacement of peaks in x-ray powder diffraction spectrograms, of the order of 2θ=0.06° (CuKα) for the (21.0) reflection from Ne$_{100}$ to Ne$_{99}$, was not sufficient for accurate measurement of composition. The position of the solvus on the nepheline side (Fig. 5) has been drawn primarily on the basis of microscopic determination of the first appearance of albite, which has certain characteristic growth habits quite distinct from that of nepheline.

**Jadeite**

The maximum pressure (45,000 psi) obtained during the present investigation was too low for the synthesis of jadeite, and the mineral never appeared in the products of the runs.

**Analcite-Water**

The system NaAlSi$_2$O$_6$·H$_2$O was investigated by Yoder (1950), who presented a transition curve, part of which was based on Morey’s data (personal communication with Dr. Yoder), for the reaction:

\[
\text{analcite}(\text{NaAlSi}_2\text{O}_6\cdot\text{H}_2\text{O}) \rightarrow \text{nepheline} + \text{albite} + \text{H}_2\text{O}.
\]

Another curve, based on revised data, was published by the same author several years later (1954). Yoder found the transition temperature to be 550° C. at 15,000 psi. The results of the present investigation suggest a somewhat lower temperature (≤530° C.) This compares favorably with Sand, Roy and Osborn’s (1957) data (525° C. at 1000 atm). The results were further verified by making a run with glass of NaAlSi$_2$O$_6$ composition at 400° C. and 15,000 psi for four days, when only analcite could form, and then raising the temperature to 540° C. and 15,000 psi, and making the run for four more days. The products of the runs indicated the presence of analcite together with clusters of albite laths. Moreover, it should be noted that the maximum temperature of stability of analcite solid solutions does not correspond to Na$_2$O·Al$_2$O$_3$·4SiO$_2$ composition, but rather to Na$_2$O·Al$_2$O$_3$·3.25SiO$_2$ composition (Saha, 1959b, Tables VIII, IX). These data have been incorporated in the triangular diagrams of Fig. 5.

**Natrolite-Water**

Runs were made at different temperatures and pressures (Fig. 6), in an attempt to synthesize natrolite (Na$_2$Al$_2$Si$_5$O$_{10}$·2H$_2$O), which has been found mostly in amygdules in basic volcanic rocks often in association with analcite and other zeolites. However, all these attempts were unsuccessful. The association of natrolite with minerals like analcite and other zeolites, calcite, etc., suggests that natrolite should be stable at relatively low temperatures and pressures. Natrolite and other zeolites are known to have been deposited in the wall-work of Roman baths at Plombieres at a temperature of 70° C. (Coombs et al., 1959). Hoss
Fig. 6. The system Na$_2$Al$_2$Si$_3$O$_{10}$.H$_2$O. Dotted lines are projections of a P-T surface, not univariant P-T curves.

\( \triangle \) — nepheline + albite,
\( \bullet \) — analcite + nepheline,
\( \bigcirc \) — analcite,
\( \square \) — zeolite “B” + species “Y,”
\( + \) — zeolite “B,”
\( [x] \) — duration of runs in days.

and Roy (1959) produced natrolite by the breakdown of Ca-type zeolite “A.” Apparently structural control plays an important part in the formation of natrolite. It was possible to convert natrolite into analcite in a long run (3 months) at 300° C. and 30,000 psi, suggesting that it is not stable at this temperature and pressure. The analcite crystals formed by the decomposition of natrolite show peak positions in the x-ray diffraction data (Fig. 2) similar to that of analcite synthesized from Na$_2$O·Al$_2$O$_3$·3SiO$_2$ glass. Assuming that the natural natrolite used for the run has the ideal composition, this suggests that natrolite was converted to analcite of its own composition, except perhaps for the amount of water that it contains.

**Albite-Water**

It has already been mentioned that long runs (3 months) were made with albite crystals at 300° C. in the presence of water vapor in order to investigate whether it can be converted to analcite of albite composition. The products of the runs did not indicate the presence of analcite. Runs (15 days) have also been made at 300° C. with mixtures of synthetic (Na$_2$O·Al$_2$O$_3$·4SiO$_2$·2H$_2$O) and natural analcites and silica in different forms, i.e., silica gel, silica glass and Ludox silica sol, in order to investigate whether any shift in the (639) peak position of analcite can be produced. Within the experimental error no shift could be detected. This makes it impossible to determine the stability of analcite solid solution, and the triangular diagrams at the low temperature region of Fig. 5 may, perhaps, represent only metastable equilibrium.
NON-TERNARY NATURE OF THE SYSTEM WHEN PARAGONITE APPEARS AS A CRYSTALLINE PHASE

As shown in Figure 5(a), (b) and (c), a three-phase field nepheline hyd- drate I—analcite solid solution-liquid (or vapor) is present. Thus in runs made with glasses within the range Na$_2$O·Al$_2$O$_3$·2.25–2.75SiO$_2$, a mixture of nepheline hydrate I and analcite solid solution (Na$_2$O·Al$_2$O$_3$ ·2.75SiO$_2$·1.5H$_2$O) would be expected. However, only analcite solid solution and paragonite could be recognized in the products, indicating that a third unrecognized phase must be present.

Microscopic examination of the charges showed no evidence of glass or amorphous material, and it was suspected that the third phase must be a vapor or a liquid which appeared as an aqueous solution after quenching (the quenched charges were observed to be wet and the liquid was alkaline). The experimental method did not permit using a large sample to collect the hydrous phase for analysis. All runs were made in sealed gold tubes and approximately equal weights of water and glass were put into the tubes, and as the hydrous phases (analcite, nepheline hydrate I and paragonite) required only a few weight per cent of water, the remaining water was present as a liquid or a vapor during the runs.

Morey and Hesselgesser (Morey, 1957a) have shown that at 2000 bars of steam pressure and at 500° C., 0.2770 of albite was dissolved by the superheated steam, and the molecular ratio of the dissolved material was that of albite, within experimental error. This confirms the fact that for the composition NaAlSi$_3$O$_8$, the composition of vapor falls within plane NaAlSiO$_4$-NaAlSi$_3$O$_8$-H$_2$O, and only one phase, albite or analcite solid solution of composition Na$_2$O·Al$_2$O$_3$·6SiO$_2$·3H$_2$O, crystallizes. No experimental results are available for any of the other phases, i.e., nepheline, nepheline hydrate I or analcite solid solution. Morey (1957) assumed that the compositions of the liquid and gas phases remain within the ternary plane for the crystallization of jadeite, nepheline and analcite. From the present investigation, it appears that this may be approximately true for nepheline, nepheline solid solution, and analcite solid solution within the range Na$_2$O·Al$_2$O$_3$·2.75–6SiO$_2$, since very little paragonite (≈1–3%) appeared in the runs. But for nepheline hydrate I and analcite solid solution synthesized from glasses within the range Na$_2$O ·Al$_2$O$_3$·2.25–2.75SiO$_2$, paragonite was present in more than trace amounts. Optical and x-ray evidence suggests that the amount of paragonite increased from ≈3% in runs made with Na$_2$O·Al$_2$O$_3$·3SiO$_2$ glass to ≈20% in runs made with Na$_2$O·Al$_2$O$_3$·2SiO$_2$ glass, and consequently the composition of the vapor changes drastically and deviates from the ternary plane.
The question now arises, can this hydrous vapor or liquid phase dissolve the excess solid materials not accounted for by the analcite and paragonite found in the charges? Table V illustrates the approximate composition of the vapor phase in the case of runs made with Na$_2$O·Al$_2$O$_3$·2·75SiO$_2$ glasses, calculated after making the following assumptions: (1) analcite solid solution of composition Na$_2$O·Al$_2$O$_3$·2·75SiO$_2$·1·5H$_2$O and paragonite crystallize from glasses within the range Na$_2$O·Al$_2$O$_3$·2·25–2·75SiO$_2$, (2) nepheline hydrate I (Na$_2$O·Al$_2$O$_3$·2SiO$_2$·H$_2$O) and paragonite crystallize from Na$_2$O·Al$_2$O$_3$·2SiO$_2$ glass, (3)

<table>
<thead>
<tr>
<th>Composition of glass (Mol. ratio)</th>
<th>Phases present after run</th>
<th>Composition of vapor (Wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$O : Al$_2$O$_3$ : SiO$_2$</td>
<td>Analcite$^1$ (95%) + Paragonite$^2$ (5%)</td>
<td>Na$_2$O 0.91%  Al$_2$O$_3$ 0.00%  SiO$_2$ 0.96%  H$_2$O 98.14%</td>
</tr>
<tr>
<td>1 : 1 : 2.75</td>
<td></td>
<td>2.89%  1.85%  0.00%  95.26%</td>
</tr>
<tr>
<td>1 : 1 : 2.50</td>
<td></td>
<td>5.00%  4.48%  0.00%  90.52%</td>
</tr>
<tr>
<td>1 : 1 : 2.25</td>
<td></td>
<td>3.39%  0.00%  0.00%  96.61%</td>
</tr>
<tr>
<td>1 : 1 : 2.00</td>
<td>Nepheline Hydrate I$^3$ (80%) + Paragonite$^2$ (20%)</td>
<td></td>
</tr>
</tbody>
</table>

1 Composition—Na$_2$O·Al$_2$O$_3$·2·75SiO$_2$·1·5H$_2$O.
2 Composition—Na$_2$O·3Al$_2$O$_3$·6SiO$_2$·2H$_2$O.
3 Composition—Na$_2$O·Al$_2$O$_3$·2SiO$_2$·H$_2$O.

about equal proportion of glass and water is assumed to be present in each case, (4) alumina, not silica, is lost in the case of glasses of composition Na$_2$O·Al$_2$O$_3$·2·25–2·50SiO$_2$.

The calculations indicate that the amount of soda, alumina and silica dissolved by the vapor is quite reasonable if one takes into account the fact that while working in the system H$_2$O-Na$_2$O·2SiO$_2$, Morey and Hesselsgesser (1952) found that at 400° C. and 2200 bars, the vapor contained 80.6% H$_2$O and 19.4% dissolved solid, and a liquid at the same temperature and pressure contained 34.0% H$_2$O, 66.0% solid. While working in the system H$_2$O-Na$_2$O-SiO$_2$-Al$_2$O$_3$, Friedman (1951) also found that liquids exist which can dissolve a fairly large amount of alumina.

It must be emphasized that Table V shows only the minimum amount of soda, alumina and silica in the vapor phase, when either silica in some cases or alumina in others has been assumed to be totally insoluble in the vapor phase. This is probably not true in the actual case, and all the
three oxides, *i.e.*, soda, alumina and silica are lost to the vapor phase to some extent.

Thus the system is no longer ternary when paragonite appears as a stable phase, as the paragonite composition falls off the NaAlSiO₄-NaAlSi₃O₈-H₂O plane in the quaternary system Na₂O·Al₂O₃·SiO₂-H₂O. At low temperatures, the runs made with glasses within the range Na₂O·Al₂O₃·2–2.75SiO₂ do not, therefore, represent ternary equilibria. It is suggested that as a result of the above calculations on the vapor composition, the alkali-rich portion of the system becomes quaternary only because of the excess vapor present during the experiments. It seems unlikely, however, that equilibrium could be attained in a reasonable time at these low temperatures if the water content of the charges were reduced to the stoichiometric amount.

**Petrological Significance of the System NaAlSiO₄-NaAlSi₃O₈-H₂O**

The non-ternary nature of the alkali-rich portion of the system NaAlSiO₄-NaAlSi₃O₈-H₂O in the presence of excess water at low temperatures (250°–500° C.) and pressures indicates that preferential solubility of soda and alumina over silica in the vapor may be an important feature, geochemically. Many alkaline rocks have been found to possess characteristic features (Smyth, 1927; Tilley, 1958), such as (1) special tectonic environment, (2) abundance of volatile constituents. Smyth (1927) contended that the volatile constituents have the power to develop alkali fractions from calc-alkali magma, but that this ability is effective only under especially favorable conditions. Tilley (1958) has discussed the metasomatic development of alkaline rocks by the process of nephelinization. From the present investigation, it seems possible that the volatiles escaping from the crystallizing alkaline rocks in a restricted range of composition may be quite enriched in soda and alumina and may be effective in the process of alkalization of the surrounding country rocks. No estimate of the importance of this process can be made until the composition of the vapor phase is known.

Paragonite appears quite frequently in runs made with glasses within the range Na₂O·Al₂O₃·2–2.75SiO₂, but it has very rarely been reported from nature (Winchell and Winchell, 1951), possibly because optically it resembles muscovite very closely. Eugster and Yoder (1954) studied 90 mica-bearing schists from the Lincoln Mountain and Hyde Park quadrangles (Vermont) by the powder x-ray diffraction method, and found that 33 samples contained paragonite in amounts up to 60% of the total mica content.

The partial determination of the extent of analcrite solid solution (anal-
cites having silica in excess of that of albite have not been investigated) indicated that information about the (1) compositions of the analcite and nepheline or albite crystals and (2) the approximate depth of burial and nature of the overlying rock formations would be helpful in estimating the temperatures attained in slightly metamorphosed rocks buried at moderate depths.

Analcite and natrolite have been reported from rocks which can be broadly classified into the following groups: (1) in igneous rocks, either as phenocrysts or in the groundmass, (2) in amygdules in volcanic rocks, and (3) in sedimentary beds.

Tyrrell (1928) has described the occurrence of analcite-syenites in the form of differentiated sills, schlierens and veins in Ayrshire along with analcite-olivine-dolerites. The schlierens and veins have been thought to have formed from the residual magmatic liquids. Where the analcite-olivine-dolerites are relatively rich in analcite, there has been only small developments of analcite-syenite, but the great development of analcite is concomitant with the impoverishment of the associated analcite-olivine-dolerite in analcites.

Tilley and Harwood (1931) have shown that vesicles in pyroxene-rich dolerites and pyroxenites from Scawt Hill were filled with thomsonite, some analcite, stilbite and natrolite. Thomsonite and analcite were also recorded in the groundmass of rocks, though never in large amounts. Tilley and Harwood concluded that these minerals in the groundmass of the rocks were formed by the alteration of the plagioclase. Larsen and Buie (1938) have described the occurrence of analcite as phenocrysts in analcite basalt from Highwood Mountains, Montana. They have been thought to have formed by primary crystallization from the magma. Roques (1947) has described the occurrence of fist-sized analcite crystals in nepheline-syenite-pegmatite on Kassa Island. Povarennyka (1954) has studied the replacement of nepheline by natrolite and albite by analcite in alkaline rocks and discussed the zeolitization of rocks during the late magmatic stage.

The commonest occurrences of analcite and natrolite in igneous rocks are in amygdules, and here there is no doubt about their secondary origin.

Extensive and comprehensive work on the occurrence of zeolites in thick sedimentary beds has been reported by Coombs (1954; Coombs in Coombs et al., 1959). He described the occurrence of thick formations of marine Triassic and late Paleozoic sedimentary beds, a total thickness of about 30,000 ft., containing several members of the zeolite group of minerals, in Taringatura District, New Zealand. Zeolites are abundantly developed here; (1) fresh analcite is common in the upper 20,000 ft., and only pseudomorphs after analcite are present in the lower 10,000 ft., (2)
members of the heulandite-clinoptilolite group are very common in the upper 20,000 ft., and diminish considerably in the lower 10,000 ft.; (3) laumontite is common only in the lower 10,000 ft. Among other minerals, the upper 20,000 ft. is rich in detrital lime-bearing plagioclase, whereas in the lower 10,000 ft. the plagioclase is albitized, with local patches of relict calcic plagioclase. Most of the albite was generated by the breakdown and hydration of calcic plagioclase to albite and laumontite. Other minerals present are prehnite, pumpellyite, etc., more common in the lower 10,000 ft. At shallow depths, analcite was formed by reaction between glass and saline waters, and with increasing depth the analcite was replaced by authigenic albite.

The occurrence of authigenic zeolites, especially analcite, in pyroclastic rocks deposited in shallow basins, has been recorded by many investigators. Tyrrell and Peacock (1926) described the occurrence of analcite associated with faujasite in alteration products of palagonite tuff. Bradley (1928, 1929) has described thin beds consisting almost wholly of euhedral analcite crystals in the Eocene Green River formation of Utah, Colorado and Wyoming. Field and microscopic evidences suggested that the analcite crystals were formed "... in place on the lake bottom as a result of interactions between various salts dissolved in the lake water and the dissolution products of volcanic ash that fell into the ancient Green River lakes." Ross (1928) has described a bed of "sedimentary analcite" from Yavapai County, Arizona, and concluded that the analcite grains were formed either (a) by the reaction between volcanic ash showers and sodium salts in the playa lakes, or (b) by the reaction between sodium salts concentrated in the playa lake and the hydrous aluminium silicates in the playa mud. Later (Ross, 1941) he supported the former possibility.

During borehole investigations of the Upper Geyser Basin of Yellowstone Park, Fenner (1936) described the frequent occurrence of analcite as distinct veinlets and as impregnations and replacement of the general mass in fragments of rhyolite and obsidian. Analcite occurs in the range 86 to 216 ft. The temperature range measured by Fenner was 115°-141° C. Heulandite, on the other hand, appears at 62 ft. and disappears at 86 ft., just above the zone of analcite. At the Weirakei thermal spring area, Steiner (cited in Coombs et al., 1959) observed that the temperature of occurrence of albite is 160°-240° C. at a depth of 100-600 m. It is interesting to note that both the temperature and depth of formation of albite here are higher than the temperature and depth of formation of analcite at Yellowstone Park. Raw (1943) concluded that analcite has been formed in palagonite tuffs in Jamaica by the reaction between the salt of the sea and silicates, especially volcanic dust under volcanic heat.
Thus a survey of the literature on “authigenic zeolites” indicates that in many cases they were formed under unusual circumstances. They were formed in sedimentary rocks (1) often composed of pyroclastic materials, (2) often under conditions of high salinity, (3) moderate temperatures, (4) and where metamorphism played any part at all, depth of burial and not stress during metamorphism was most important. Comparison with the conditions of laboratory investigation of the system NaAlSiO₄-NaAlSi₃O₈-H₂O brings out several points of interest. Analcite crystallizes readily from most of the glasses used as starting materials for the runs, and appears to be very stable at low temperatures, and in cases of particular compositions deficient in silica is stable even up to 560° C. at 15,000 psi. This would suggest that low temperature metamorphism of volcanic rocks would give rise to analcite and other zeolites, as in the case of laboratory experiments. This is in complete accord with the field occurrences of “authigenic” zeolites, described in the previous paragraphs. Moreover, with increasing temperature and pressure, i.e., increasing depth of burial, we would expect analcite to be replaced by albite, and this has been found to be the case in New Zealand (Coombs, 1954). As regards salinity, water extracted from the gold tubes after the experimental runs was found to be quite alkaline, though the pH was not measured. Barrer and White (1952) measured the pH of solutions after making runs with gels of compositions Na₂O·Al₂O₃·nSiO₂ in the presence of water only, and they also found that the solutions were quite alkaline, the pH decreasing with rise in temperature (10.0 at 150° C. and 7.4–7.0 at 450° C.). This is probably due to the leaching of some soda from the glasses, as mentioned before.

Authigenic zeolites have also been found in sedimentary beds which may or may not have been derived from volcanic ash. Rengarten (1940) found authigenic analcite deposited around fragments of decomposed porphyrite in Permian sandstones from Russia and as minute crystals in the gypsum and carbonate matrix. It was considered to have been formed during the deposition of the sandstone. Foster and Feicht (1946) have described sulfur balls from the Pittsburgh coal seam in West Virginia containing analcite, pyrite and other minerals. They concluded that calcium bicarbonate solutions percolating down from the overlying limestones might have neutralized the acids and given rise to analcite from clay-like minerals. The presence of pyrite instead of marcasite indicated alkaline conditions. Keller (1952) found it more probable that authigenic analcite in the Popo Agie member of the Chugwater formation was formed by the reaction of strong sodium-rich carbonate-sulfate solutions with clays under an oxidizing alkaline environment. A volcanic origin of the parent material was not acceptable because of the complete absence
of volcanic material, and the presence of fossil *Unio* of freshwater type suggested the absence of strongly saline environment. Van Houten and Olson (1957) have described argillites from Upper Triassic Lockatong Argillite composed of analcite and illite, and contended that analcite in samples from widely separated outcrops suggests that the mineral is authigenic.

**Conclusion**

The present study thus indicates the importance of determining the composition of natural analcites of varying modes of origin. Given this information, and if reasonable assumptions as to the pressures are made, it is possible to fix the temperatures at which any given analcite may have been formed. In the case of the more sodic analcites, which may be expected to occur as alteration products in feldspathoidal rocks, reversal of reaction has been achieved and the reaction curve experimentally determined may represent equilibrium conditions. Reversal of reaction has not been achieved for the more siliceous analcites, but the apparent transition boundary may probably represent an upper temperature limit for the stability of these analcites.

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