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ANALCITE-ALBITE EQUILIBRIA AT LOW TEMPERATURES

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ABSTRACT. The reaction analcite + quartz = albite + H_2O (1) has been investigated in the range 130° to 250°C at 2 to 6 kb PH_2O, using a reaction-rate method involving the weight change of quartz or albite crystals. The data suggest equilibrium at 190 ± 10°C at 2 kb, 170 ± 10°C at 4 kb, and 4.75 ± 0.5 kb at 150°C ($PH_2O = P_{total}$).

The equilibrium curve has negative slope at higher pressures and intersects the slope for the reaction albite = jadeite + quartz (3) in the region 50° to 120°C at PH_2O between 5 and 6.5 kb. These data suggest that the univariant relation between analcite and jadeite must have a *positive* slope.

Single quartz crystal experiments on the reaction heulandite = laumontite + quartz + H_2O (5) give an indication of equilibrium in the range 120° to 140°C at 2 kb PH_2O. It is considered that these data are not satisfactory enough to bracket the equilibrium further. The intersection of the slopes for (1) and (5) in the region 175° to 210°C and 1.5 to 2 kb PH_2O indicate that negligible amounts of erosion have affected the sedimentary sequence at Taringatura, New Zealand.

INTRODUCTION

Several experimental studies in the system Na_2O–Al_2O_3–SiO_2–(H_2O) have provided useful limiting data on the stabilities of the naturally occurring minerals analcite (An), albite (Ab), jadeite (Jd), and nepheline (Ne).

Field studies of assemblages containing these minerals are well described in the literature. The observations of Coombs (1954) and Coombs and others (1959) on material from graywacke piles in New Zealand suggest that analcite may become unstable relative to albite at quite low temperatures and pressures. The reaction

$$\text{analcite} + \text{quartz} = \text{albite} + H_2O \qquad (1)$$

is considered to give useful limiting data on the stabilities of natural assemblages.

Previous experimental studies have outlined the difficulties in obtaining an equilibrium boundary for reaction (1). These include the metastable crystallization of analcite (Ellis, ms; Campbell and Fyfe, 1965) and the possible existence of a range of analcite compositions (Saha, 1959, 1961).

THE COMPOSITION OF SYNTHETIC ANALCITE

The recent studies of Boettcher and Wyllie (1969) and Hamilton (ms) support the earlier observations of Saha (1959), Greenwood (1961), and Peters, Luth, and Tuttle (1966) in noting that the compositions of analcites synthesized from oxide-mixes or gels do not always satisfy the stoichiometric requirements of the conventional formula ($NaAlSi_2O_6.H_2O$). Both silica-rich and silica-poor varieties are believed to occur. It is possible that many of these forms are the metastable products of runs of short duration. It is not yet known if they will revert to a composition nearer $NaAlSi_2O_6.H_2O$ in longer runs.

In the previous syntheses of analcite, the starting materials were generally prepared with anhydrous compositions on the binary join Ab-Ne. If the phases produced are stoichiometric with respect to Na:Al, then we are concerned with planes in the ternary system Ne–Q–H_2O (V). Therefore we can have two solid phases in equilibrium with a vapor at arbitrary P, T. By fixing either P or T we can have three solid phases in equilibrium with a vapor. However, if any of the synthesized phases have compositions with ratios other than Na:Al (for example paragonite) the system becomes quaternary. Here, we can have three solid phases coexisting with a vapor at equilibrium, at arbitrary P, T (compare Morey, 1957).

In the assignment of composition to a synthesized phase, based solely upon the composition of the starting material, we must have 100 percent yield of that phase in order to assign unequivocally that composition. The appearance of small amounts of paragonite in the syntheses by Saha (1959) and Hamilton (personal commun.) may suggest that the system is not ternary. Upon this basis we are not justified in assigning the bulk composition to the analcite, however trivial the divergence. Similarly the determination of the composition of analcite, using the form of the Ab-Ne phase diagram in conjunction with visual (or X-ray) estimates of the percentages of the synthesized phases, may not be justified if the system is not ternary. The divergence may be slight but sufficient to mask the true composition.

THE COMPOSITION OF ANALCITE AND PHASE RELATIONS

The systematic studies of natural analcite composition by Wilkinson and Whetten (1964) and Coombs and Whetten (1967) indicate that natural analcites may exhibit compositional variation over the same range as their synthetic analogues. This evidence supports the suggestion that non-stoichiometric compositions may well be stable.

Obviously the possible stability of compositional variants may significantly affect the univariant relations between phases. We may consider three major cases of varied analcite composition and discuss the particular reactions associated with each.

Primary igneous analcites range in composition from silica-poor (with anhydrous compositions between Ne and Jd (An_I)) to near stoichiometric (anhydrous Jd composition (An_{II})). Sedimentary and "burial metamorphic" analcites range from An_{II} to silica-rich compositions (anhydrous between Jd and Ab (An_{III})). An examination of figure 1 reveals the following possible univariant relations.

Case A. Silica-poor analcite (An_I)

$$\begin{aligned} An_I &\rightarrow Jd + Ne + V \\ Ab + An_I &\rightarrow Jd + V \\ Q + An_I &\rightarrow Ab + V \\ An_I &\rightarrow Ab + Ne + V \end{aligned}$$

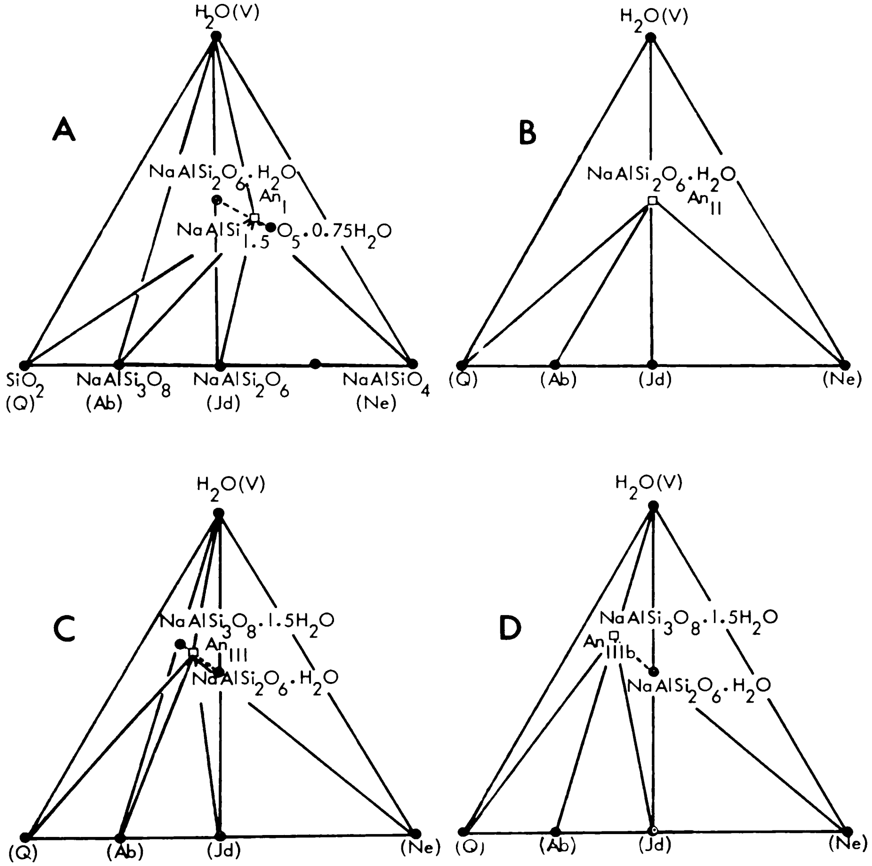


Fig. 1. Phase relations in the system $NaAlSiO_4$(Ne)–SiO_2(Q)–H_2O(V).

Case A. Silica-poor analcite (An_I) with analcite composition between $NaAlSi_{1.5}O_5.0.75H_2O$ and $NaAlSi_2O_6.H_2O$.

Case B. Stoichiometric analcite (An_{II}) with anhydrous composition $NaAlSi_2O_6$(Jd).

Case C. Silica-rich analcite (An_{III}) with analcite composition between $NaAlSi_2O_6.H_2O$ and $NaAlSi_3O_8.1.5H_2O$.

Case D. Silica-rich analcite (An_{IIIb}) with anhydrous composition $NaAlSi_3O_8$ (Ab).

For the sake of clarity solid-solution of the anhydrous phases has been ignored.

Case B. Stoichiometric analcite (An_{II})
$An_{II} \rightarrow Jd + V$
$Q + An_{II} \rightarrow Ab + V$
$An_{II} \rightarrow Ab + Ne + V$

Case C. Silica-rich analcite (An_{III}), anhydrous composition between Ab and Jd
$An_{III} \rightarrow Jd + Q + V$
$An_{III} \rightarrow Ab + Jd + V$
$An_{III} \rightarrow Ab + Ne + V$
$Q + An_{III} \rightarrow Ab + V$
$Ne + An_{III} \rightarrow Jd + V$

There is also a special case (D) corresponding to an analcite having the anhydrous composition of Ab.

$$\mathrm{An_{IIIb} \rightarrow Jd + Q + V}$$
$$\mathrm{An_{IIIb} \rightarrow Ab + V}$$
$$\mathrm{Ne + An_{IIIb} \rightarrow Jd + V}$$

The reactions

$$\mathrm{Ab + Ne \rightleftharpoons Jd} \tag{2}$$

and

$$\mathrm{Ab \rightleftharpoons Jd + Q} \tag{3}$$

are independent of analcite composition. The reaction An $\rightleftharpoons$ Ne + Q + V will clearly be metastable.

The reactions

$$\mathrm{An \rightleftharpoons Ab + Ne + V} \tag{4}$$

and

$$\mathrm{An + Q \rightleftharpoons Ab + V} \tag{1}$$

are limiting reactions for the stability of analcite (unless the analcite has the anhydrous composition of Ab—see case D in fig. 1).

If the *stable* analcite at high temperatures (in the absence of quartz) is silica-poor, then a stoichiometric analcite ($\mathrm{An_{II}}$) subjected to P, T conditions near the boundary An $\rightleftharpoons$ Ab + Ne + V (4), will decompose to the stable silica-poor analcite *plus* albite. Similarly, if the analcite stable at low-temperatures, in equilibrium with albite and quartz, is more silica-rich than $\mathrm{An_{II}}$, then we expect a divariant field of analcite solid-solution *plus* albite between the two limiting reactions (1) and (4).

So far we have little data on the stability of analcite solid-solutions, but detailed analyses of analcites from progressive metamorphic terrains may suggest relations such as:

$$\mathrm{An_a \rightarrow An_b + SiO_2 + \ldots\ldots\ldots\ldots}$$

Solid solution of the anhydrous phases is not considered to be significant over the range of conditions under discussion.

SOLUBILITY OF THE PHASES AND THE EQUILIBRIUM BOUNDARY

In addition to chemical compositional differences which may affect the real position of the stability field of analcite, there will undoubtedly be kinetic factors which may affect the apparent synthesis boundaries. The use of a quartz crystal as a reaction monitor, in the present experiments, may obscure some kinetic factors. Natural analcite, close to $\mathrm{NaAlSi_2O_6.H_2O}$, has been used in the present experiments, and it is assumed that this is near the stable analcite composition for low temperature equilibrium. If the more stable analcite at these pressures and temperatures were silica-poor (unlikely since silica-poor types are generally of igneous origin representing higher temperatures), then the weight-gain of the quartz crystal may not be due solely to albite breakdown but also to the formation of a more stable silica-poor analcite. Similarly the weight-loss of the quartz crystal may not be due solely to albite growth but to the formation of a more stable silica-rich analcite. This latter case is more likely, since sedimentary and "burial metamorphic" analcites (presumably forming at lower temperatures than igneous analcites) often show silica enrichment over $NaAlSi_2O_6.H_2O$.

The use of albite crystals as reaction monitors (compare Campbell and Fyfe, 1965) precludes the uncertainty in quartz solution/growth interpretation. Therefore the solution of albite may serve as a much closer indicator of equilibrium than the growth of analcite or quartz. The experiments in the present study, at 2kb PH_2O, involved the use of both quartz and albite as a reaction monitor. It can be seen from figure 2A that the crossover in the weight-change of albite crystals intersects the crossover in the weight-change of quartz crystals within the limit of measurement. This is taken to indicate that the analcite composition used in the present experiments is near to the stable analcite composition under these P, T conditions.

EXPERIMENTAL STUDY

Natural minerals were used in all experiments.

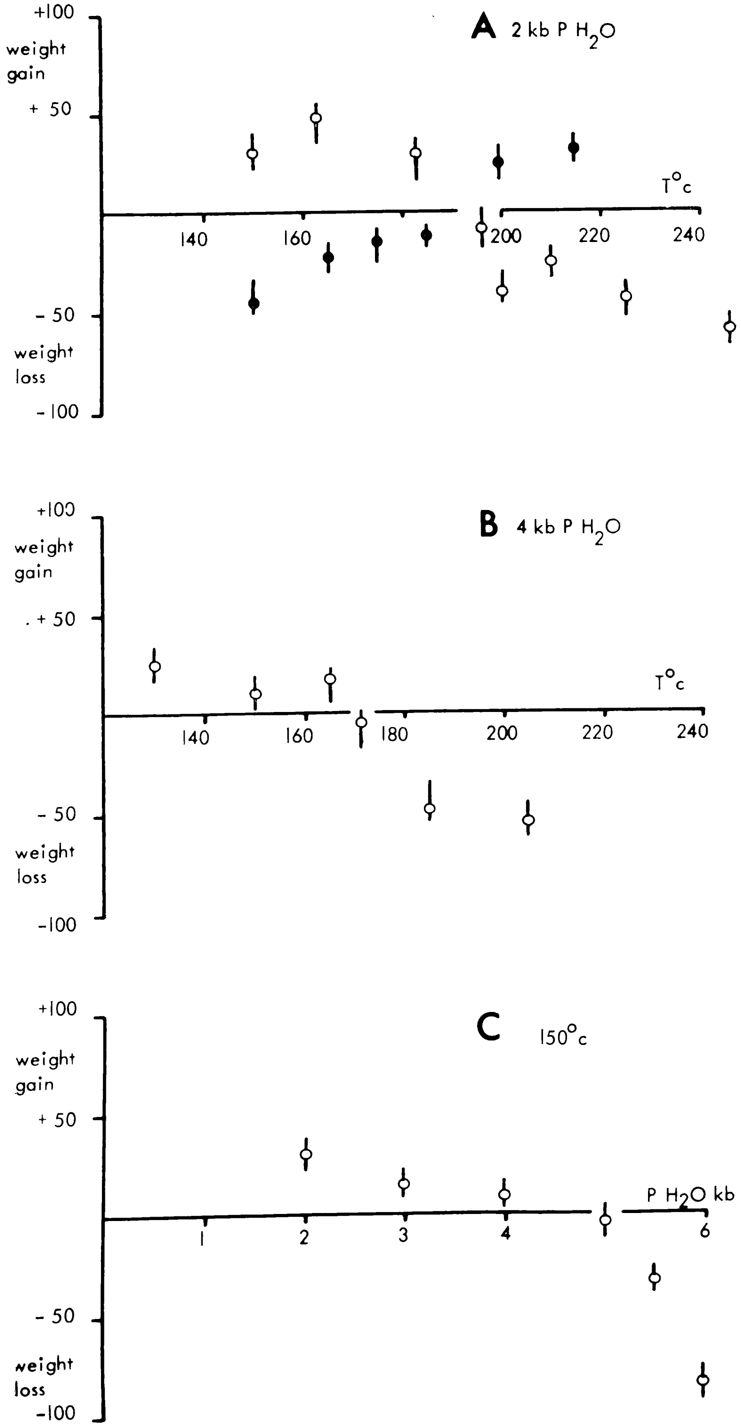
Analcite from Table Mountain, Golden Colorado. This sample is from the same locality as the material used by Yoder and Weir (1960) for compressibility studies and King (1955) for thermochemical studies. Yoder and Weir report an analysis for this material by E. H. Oslund, which reduces to the formula $(Na_{0.95}Mg_{0.01})(Al_{0.96}Si_{2.04})O_6.0.98H_2O$. No excess quartz was observed in microscopic examination of the sample used here.

Albite from Amelia County, Virginia (low albite).

Quartz clear crystals of high purity, cut in a manner described previously (Thompson, 1970).

A 50:50 by weight mixture of analcite and albite was ground to size less than 300 mesh. Three one hundredths of a gram of the mixture was sealed in a gold capsule of constant volume with 0.05 g of deionized water and a quartz crystal (about 1.5 cm long by 0.25 cm diam). The technique has been described in a previous paper (Thompson, 1970). Runs were of two weeks duration.

A slight modification to the previous weighing procedure has been developed. In the preliminary experiments it was noted that the weight-changes of the quartz crystals were only of the order 10 to 50 μg for runs of two weeks duration. These figures are near to the limit of accuracy of the method. Since slight temperature and humidity variation can change balance characteristics and increase the errors, tares of platinum wire were prepared. These were cut so as to be about $\pm$ 50 μg from the initial weight of the crystal. The weights of the quartz crystals were compared directly with the weights of the tares, before and after each experiment. From an average of six weighings it was found that the range of error in weight-change of the quartz crystal (compared to a fixed weight of the platinum tares) was not always symmetrical about an arithmetical mean. The skewness of the error bars in figure 2 illustrates this point. Such procedures should improve the accuracy of the method and eliminate any doubt as to the effect of temperature or


A 2 kb P H2O
+100
weight gain
+ 50
- 50
weight loss
- 100
T°c
140
160
200
220
240
B 4 kb P H2O
+100
weight gain
+ 50
- 50
weight loss
-100
T°c
140
160
180
200
220
240
C 150°c
+100
weight gain
+ 50
- 50
weight loss
-100
P H2O kb
1
2
3
4
6

humidity on balance performance. Comparison with a standard quartz crystal of similar dimensions eliminates sample inaccuracies due to surface adsorption of water.

The weight-changes of quartz crystals are shown by open circles in figure 2. The data suggest crossovers at 190 ± 10°C at 2 kb, 170 ± 10°C at 4 kb, and 4.75 ± 0.5 kb at 150°C ($PH_2O = P_{total}$).

Experiments were conducted at 2 kb PH_2O using weighed crystals of Amelia albite with powdered analcite plus quartz. The conditions were the same as in the quartz crystal experiments. The results are shown by closed circles in figure 2A. It can be seen that these points indicate a crossover at 185 ± 10°C. These points intersect the quartz weight-change crossover within the limits of accuracy. We may conclude that the stable analcite composition in equilibrium with albite and quartz at these P,T conditions must be near the composition of the analcite used in the experiments. If the stable analcite composition under these conditions is only slightly different from the one assumed here (An_{II}), the method is not sensitive enough to restrict it further. The weight-loss of the albite crystals is a more important indicator of equilibrium. We cannot be sure that the weight-gain of the crystal represents the growth of *low* albite. In a preliminary experimental investigation of analcite solid solutions, the analcite powder was run with a quartz crystal and excess water, at 180°C at 2 kb P H_2O for two weeks. A weight-change of less than $-$ 10 μg, which lies within the limits of precision of weighing, was observed. This gives much more significance to the conclusion that the analcite composition used in the experiments is close to the stable analcite composition under these conditions.

THE ANALCITE-ALBITE EQUILIBRIUM CURVE

The resulting equilibrium curve for reaction (1) at the condition $PH_2O = P_{total}$ is shown in figure 3 as A-B. The point A is Campbell and Fyfe's (1965) equilibrium point at about 190°C at 12 atm water pressure. Their curve A-C is based on thermodynamic extrapolation. While the present data broadly conform the shape and position of their equilibrium curve, the present data suggest $\Delta G^\circ = 0$ at 25°C between 5 and 6 kb, compared with Campbell and Fyfe's estimated value of 4200 atm. However the values used by these authors depend heavily upon an estimate of ΔG°_{298} from entropy values which yield a ΔS°_{298} of as little as + 1 eu.

The calorimetrically determined heat capacity of analcite may be compositionally dependent. The sample used by King (1955) in his heat capacity determinations is slightly silica-rich yielding a formula of 96.5 percent analcite, 3.3 percent SiO_2.0.2 percent H_2O. Attempts to calculate the effect of varying silica content on the thermal stability of analcites

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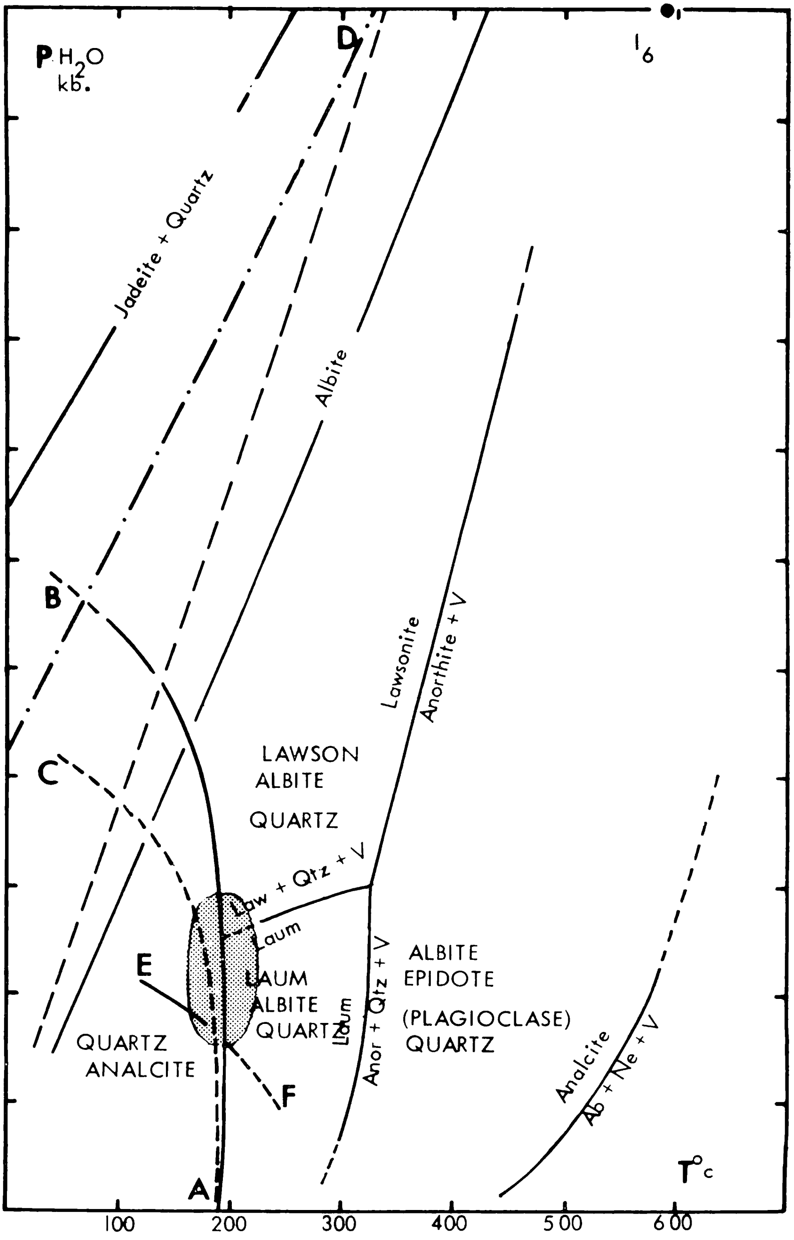
Fig. 2. Plots of weight-change of crystals for the reaction $An + Q \rightleftharpoons Ab + H_2O$. The weight-change in micrograms is plotted against temperature or pressure. The open circles represent weight-change of quartz single crystals. The closed circles in A represent the weight-change of albite crystals.


P_{H_2O}
kb.
I6
0
9
8
7
6
5
4
3
2
1
100
200
300
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500
600
$T^{\circ}c$
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Jadeite + Quartz
Albite
Lawsonite
Anorthite + V
LAWSON
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ALBITE
QUARTZ
Laum
Anor + Qtz + V
ALBITE
EPIDOTE
(PLAGIOCLASE)
QUARTZ
QUARTZ
ANALCITE
Analcite
Ab + Ne + V

were not satisfactory. In order to evaluate this effect fully, we would need to have heat capacity measurements on analcites known to be of different composition. Such measurements would require extremely accurate determination in order to lend any significance to the orginally small values of ΔS° and ΔG°.

The estimation of ΔG°_{298} from the ΔS_T in the range 190° to 25°C relies upon the assumption that the entropy change of zeolite-feldspar reactions are directly comparable with other silicate dehydrations. This may lead to errors of the order of 100 percent for ΔS_T, which may considerably alter the estimate of ΔG°_{298}. King and Weller (1961) determined the heat capacity value for dehydrated analcite and concluded that the measured ΔS°_{298} values for analcite and dehydrated analcite of 14.1 eu was unusually large for one mole of water difference in composition.

In fact the correspondence between the calculated values and the present experimentally determined values are extremely good when one considers the paucity of thermochemical data and the distances of extrapolations involved. If the values of the present experimental points are accepted then it is possible to estimate better values of ΔG°_{298} and ΔS_T for the reaction (1).

ANALCITE–ALBITE–JADEITE RELATIONS

The net result of the displacement of the equilibrium curve for reaction (1) to higher pressures is that the intersection with the equilibrium curve for the reaction Ab $\rightleftharpoons$ Jd + Q (3) may lie within an experimentally realizable position in P,T space. This reaction (3) has not been investigated at lower temperatures—in fact in the P,T region where it is believed to occur naturally, in glaucophane lawsonite metamorphism. The position of this equilibrium curve in the P,T region of interest relies upon extrapolation from higher pressure and temperatures. The four curves shown in figure 3 are from Hlabse and Kleppa (1968) and indicate the range of extrapolations from higher pressures and temperatures. The lower two curves are calculated curves based upon entropy

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Fig. 3. P-T diagram for univariant equilibria mentioned in the text. A-B is the equilibrium curve for analcite + quartz $\rightleftharpoons$ albite + H_2O as determined in this study.

A-C is Campbell and Fyfe's (1965) curve for the same reaction.

B-D is the extrapolation by Newton and Smith (1967) from their high pressure equilibrium studies for the reaction Ab = Jd + Q. The other curves for this reaction are from Hlabse and Kleppa (1968).

E-F is the estimated equilibrium curve for the reaction heulandite $\rightleftharpoons$ laumontite + quartz + H_2O.

The shaded region represents pressures and temperatures inferred from Coombs (1954) observations at Taringatura, New Zealand.

I_6 is the invariant point An/Ab/Jd/V/L from Boettcher and Wyllie (1969).

The curve An $\rightleftharpoons$ Ab + Ne + V is from Greenwood (1961). Only subsolidus relationships have been considered here. The curves relating laumontite, lawsonite, anorthite are from Thompson (1970).

The stability fields of assemblages important in low-grade metamorphism are indicated. The stability fields of assemblages containing aragonite, calcite, jadeite, wairakite, et cetera have not been considered here.

of ordering corrections on a disordered albite. It is likely that these curves will not represent the natural situation, since the form of albite in glaucophane-lawsonite metamorphism is low albite with no signs of inversion. The dot-dash curve represents the calculated value for low albite and corresponds well with Newton and Smith's (1967) extrapolation from high pressure equilibrium studies.

If the present data for reaction (1) are accepted, then a precise location of reaction (3) may be possible in the low pressure region, if it is possible to locate the univariant curve for the reaction relating analcite and jadeite.

It was mentioned earlier that varying analcite composition will not affect the nature of the two limiting reactions (1) and (4). The composition of analcite under consideration will strongly influence the actual univariant relations between analcite and jadeite. In the case of a stable silica-poor analcite, perhaps of the composition suggested by Greenwood (1961) $Na_{1.07}Ai_{1.07}Si_{1.93}O_6.H_2O$, the univariant relation between analcite and jadeite will be of the form Ab + An $\rightleftharpoons$ Jd + V. The relation in this form has been considered by Boettcher and Wyllie (1969) and Ryabchikov and Hamilton (ms).

Clearly the determination of the equilibrium boundary for reaction (1) in this study indicates that the reaction An + Q $\rightleftharpoons$ Ab + V (1) will intersect the slope of the reaction Ab $\rightleftharpoons$ Jd + Q (3), according to Newton and Smith (1967), in the region 50° to 120°C at PH_2O between 5 and 6.5 kb. For the analcite composition An_{II} the univariant relation between analcite and jadeite will be An $\rightleftharpoons$ Jd + V. It is considered that if an analcite composition other than $NaAlSi_2O_6.H_2O$ (as assumed here) is stable, the invariant point will not be significantly displaced. Nevertheless this difference in composition will not be sufficient to allow the general reaction between analcite and jadeite to have a negative slope, as proposed in the diagram by Boettcher and Wyllie (1969, p. 897, fig. 8).

Ryabchikov and Hamilton (ms) have also located the invariant point I_6 of Boettcher and Wyllie (1969) and argue from thermodynamic calculations that the univariant relation between analcite and jadeite must have a positive slope (compare Fyfe and Valpy, 1959).

The recent results of Manghnani (1970) confirmed the earlier results of Newton and Kennedy (1968) in the location of the analcite-jadeite relation very close to that indicated in the above discussion. Especially of interest is the occurrence of trace albite with analcite in the high temperature (and high pressure) runs, whereas his data indicate the growth of analcite only at lower temperatures (and lower pressures).

Clearly if the high temperature relationship between analcite and jadeite involves a stable silica-poor analcite, then the reaction will be of the form Ab + An $\rightleftharpoons$ Jd + V and will be divariant if the original analcite composition differs from the stable one. At lower temperatures, if the stable analcite composition is $NaAlSi_2O_6.H_2O$ then the univariant relation will be of the form An $\rightleftharpoons$ Jd + V. Again a divariant region will exist if the analcite does not have this composition. Therefore the relation between analcite and jadeite cannot be a straight line in P,T space and is expected to be convex upward between I_6 and the stable intersection of (1) and (3). It is unfortunate that the relation between analcite and jadeite, which has been of much interest in experimental and theoretical phase equilibrium studies, does not have widespread application in nature. It seems to be only directly applicable to analcite-jadeite pods in some serpentinites.

Other phases may influence the position of the analcite-jadeite equilibrium curve. If other silica-rich phases are stable, then this will reduce the analcite + quartz stability field, possibly even making analcite-jadeite relations metastable. It is unlikely that silica-poor phases will influence the stability of analcite *plus quartz*, although such phases may well be stable at low pressures and temperatures in a silica-poor system.

The stability fields for diagnostic mineral assemblages in low-grade metamorphism are indicated in figure 3. The data for laumontite, lawsonite, and anorthite stabilities are from Thompson (1970). The assemblage albite plus epidote reacts to form plagioclase with increasing temperature. Additional assemblages containing aragonite or jadeite can be added to those presented here.

HEULANDITE-LAUMONTITE RELATIONS AND THE ANALCITE-ALBITE BOUNDARY

It was noted by Coombs (1954) and Coombs and others (1959) that in sedimentary piles at Taringatura, New Zealand, analcite was not observed in rocks below about 17,000 feet (below the present stratigraphic level)—its place being taken by albite. Heulandite persists to slightly greater depth, giving way to laumontite (plus quartz), probably via some reaction as:

$$\text{heulandite} \rightarrow \text{laumontite} + \text{quartz} + \text{vapor} \qquad (5)$$

This reaction must occur near (1) since the assemblage analcite + heulandite + quartz gives way to albite + laumontite + quartz. The intermediate assemblages analcite + laumontite and heulandite + albite occur only locally. Coombs and others assume that not more than 10,000 feet of sediment could have been removed by erosion since the metamorphism. Therefore the pressure of formation of albite from analcite via reaction (1) must lie in the pressure range 1.5 to 3 kb for $PH_2O = P_{total}$. Therefore, the univariant curve for the dehydration reaction (5) would be expected to intersect the analcite-albite curve in the shaded region in figure 3.

EXPERIMENTS ON THE HEULANDITE-LAUMONTITE REACTION

Single crystal experiments were conducted using a quartz crystal and a 50:50 by weight mix of heulandite and laumontite plus water. The heulandite was from Theigarhorn, Iceland, and the laumontite from Pine Creek, Calif. (see Thompson, 1970). The runs were conducted at 2 kb PH_2O for two weeks. The results are indicated in figure 4. From the disposition of the circles it can be seen that the weight-changes of the quartz crystals were surprisingly small and lie very near the limits

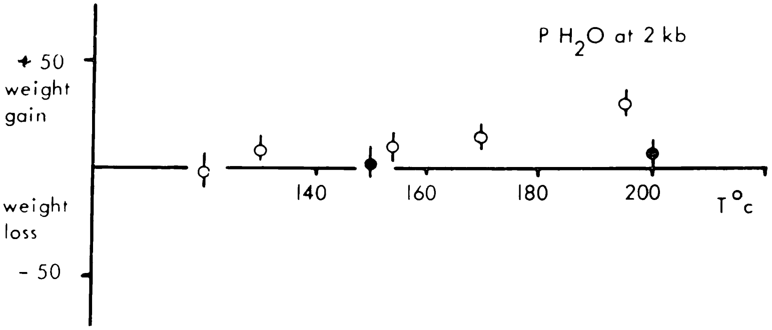

Fig. 4. Plot of weight-change of quartz crystals for the reaction heulandite $\rightleftharpoons$ laumontite + quartz + H_2O against temperature, for 2 kb PH_2O. The closed circles are results obtained for a sample of heulandite from Montecchio Maggiore, Italy. The open circles are results obtained for a sample from Theigarhorn, Iceland.

of accuracy of the method. At best the data indicate equilibrium in the range 120° to 140°C for 2 kb PH_2O. The data cannot be considered unequivocally to set the equilibrium temperature. Nor was the crossover in the weight-change of the quartz crystals obtained to any degree of satisfaction. However from the distribution of these zeolites in natural hydrothermal systems, measured geothermal gradients indicate that reaction (5) may occur in the temperature range 80° to 140°C (Steiner, 1968; Seki and others, 1969). If we may *assume* equilibrium in this temperature range, near 120°C, then estimates of the slope for reaction (5) based upon poor thermodynamic data suggest that it will be strongly negative under these conditions. The slope (represented by E-F in fig. 3) will pass through the lowest part of the shaded area representing the coincidence of analcite-albite relations with heulandite-laumontite relations. If this data were correct, then it would indicate negligible amounts of erosion at Taringatura.

There are several possible reasons to explain the very small weight-changes of the quartz crystals in the heulandite-laumontite experiments. Slow reaction rates at the low temperatures of the investigation may allow only limited reaction for the percentages of phases in the original starting mix. The heulandite from Iceland was known to contain appreciable Na in the analysis. This raises the possibility that the breakdown of natural heulandite may not necessarily follow reaction (5). In fact small amounts of analcite (or wairakite?) were observed among the products of the run at 195°C at 2 kb. This suggests that the reaction may actually be:

$$\text{heulandite}_{a\,(\text{Ca-Na bearing})} \rightarrow \text{heulandite}_{b\,(\text{Na-depleted})}$$
$$+ \text{ Na-bearing phases (analcite or albite)}$$

followed by:

$$\text{heulandite}_b \rightarrow \text{laumontite} + \text{quartz} + \text{vapor}$$

at higher temperatures. Such possibilities may be revealed by systematic analyses of heulandites in progressive metamorphic sequences.

A heulandite sample from Montecchio Maggiore, Italy, known to contain less Na than the previous sample, was run in the same manner at 150° and 200°C at 2 kb PH_2O for two weeks. No analcite was observed in the charges after the runs. These results show even smaller weight-change of the quartz crystals in the same interval (closed circles in fig. 4).

The common natural association of heulandite with relict volcanic glass or amorphous forms of silica may suggest a compositional range of heulandite with regard to SiO_2, in the same manner as proposed for analcite. This may have some bearing on the trivial amounts of reaction in the above experiments in the presence of quartz.

Clearly the estimate of the dP/dT for reaction (5) depends upon the entropy of heulandite. This figure was calculated from basic thermodynamic data for the formula $CaAl_2Si_7O_{18}.6H_2O$. Obviously since heulandites can possess variable SiO_2 and H_2O (Wise, 1967), this estimate may be in error. Moreover in a recent paper, Breger, Chandler, and Zubovic (1970) suggest that this formula for heulandite may be much in error especially with regard to H_2O content. They suggest the formula should be $CaO.Al_2O_3$. (6 or 7) $SiO_2.2H_2O$. If this were the case then reaction (5) would not hold, and we would need to consider a reaction of the type:

$$\text{heulandite} + 2H_2O \rightarrow \text{laumontite } (CaAl_2Si_4O_{12}.4H_2O) + (2 \text{ or } 3)\ SiO_2$$

It is unlikely that this reaction applies in the zeolite zones, which give a fairly good impression of progressive dehydration with increasing pressure and temperature.

It is unlikely that the PH_2O was much less than P_{load} at Taringatura, since any reduction of water pressure would restrict the formation of analcite plus quartz to very shallow depths.

The effect of a multicomponent fluid phase on the analcite-albite equilibria has not been considered in this study. The effect of an $H_2O:CO_2$ fluid phase on zeolite-carbonate equilibria will be discussed elsewhere.

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