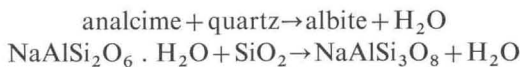volcanic debris which occurs in the southern part of New Zealand. The volcanic material was originally partly crystalline and partly glassy. Such material would absorb and retain large quantities of water. Many new minerals formed during the burial and heating of the material, in particular silicates of the zeolite family.

The total pile has an estimated thickness of about 10 km and there is good evidence that the cover overlying this was never very great, perhaps not as much as 3 km. At about the centre of the pile a simple reaction occurs:

$$\text{analcime} + \text{quartz} \rightarrow \text{albite} + H_2O$$
$$NaAlSi_2O_6 \cdot H_2O + SiO_2 \rightarrow NaAlSi_3O_8 + H_2O$$

Obviously, if we knew the conditions of this reaction exactly, we would also know something about water pressure and temperature in the environment.

Now as the reaction occurs at a depth of about 5–8 km, one would guess that the temperature of reaction must be in the range 100–200°C. Silicates are not the most reactive of substances so we might expect that this reaction could be difficult to study at this low temperature. We also know a little of the thermo-dynamics of this reaction. Thus if the water is in the liquid state, the entropy of reaction at 25°C is only $+1$ cal mol^{-1} deg^{-1} (1 entropy unit, e.u.) and at 200°C will only be about 3 e.u. At equilibrium the free energy change of the reaction (free energy measures the chemical driving force) is zero, and even 100° from equilibrium will only be 200–300 cal mol^{-1}. If we compare these numbers with those for most common inorganic reactions, they are quite trivial. This means that as the affinity of the reaction is near zero even a long way from equilibrium, then reaction may hardly occur at all, at least in a short time.

Some workers tried to find the conditions of the reaction by studying the growth of the minerals from reactive materials such as a glass or mixtures of reactive oxides. Such experiments only showed that the zeolite analcime could nucleate and grow at temperatures which are clearly unrealistic. Where albite or analcime appeared in the experiments this was simply a reflection of reaction rates.

A chemist might think of using calorimetric techniques to find equilibrium. Thus if we could measure the heat of reaction, and given the entropies of the phases, we could use the laws of thermodynamics to obtain positions of equili-brium. It turns out that the accuracy required in such measurements far exceeds anything yet achieved in such techniques. We must resort to some direct study.

If we place a mixture of albite–quartz and analcime in water at some randomly chosen P and T, some phases should grow and some should vanish. By using the mixture we have eliminated nucleation barriers, and only growth barriers remain. Rates of solution of most minerals are quite rapid and seldom control the rate of a reaction. In the present case, the rate is still so slow, that with available techniques for measuring the amounts of crystalline phases in a mixture, reaction can hardly be detected at low temperatures. We can improve this one step further. If we use a mixture of powdered albite and analcime and a single

crystal of quartz, we can focus all reactivity of quartz on one single crystal. We can weigh this very accurately with a micro balance and find out if the crystal is growing or dissolving. Trivial amounts of reaction can be measured. Using this technique Campbell & Fyfe[4] found a phase diagram as shown in Fig. 5 below. It will be noted that analcime has a rather odd field of stability. It can be dehydrated by raising water pressure. This effect arises from the very large molar volume of the hydrate relative to the dehydration product. If we draw on this diagram geothermal gradients corresponding to $10–30°$ km^{-1} we observe that the reaction should occur at $P \simeq 3$ kb, depth $\simeq 11$ km, $T \simeq 115°C$ for $10°$ km^{-1} gradient, and at $P \simeq 1200$ bars, depth $\simeq 4\cdot5$ km, $T \simeq 180°C$ for a geothermal gradient of $30°$ km^{-1}. Relating this to the field occurrence, it seems that $10°$ km^{-1} is too low a gradient and $30°$ km^{-1} a little high; $20°$ km^{-1} would account for the observations.
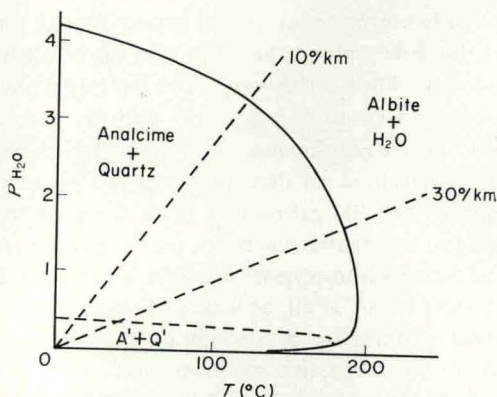

Fig. 5. Stability field of analcime+quartz. The full line corresponds to condition, $P_{H_2O} = P_{Total}$. The dashed line indicates the approximate reduction of this field when $P_{H_2O} \simeq \frac{1}{3} P_{Total}$. Geothermal gradients of $10°$ and $30°$/km are indicated.

But what would happen if P_{Load} was not the same as P_{H_2O}? The reaction is occurring at rather shallow depths and it may well be that the condition $P_{H_2O} \simeq \frac{1}{3} P_{Load}$ may be more applicable. The reaction has not been experimentally studied under these conditions but it is possible to calculate the results by thermodynamic methods. The analcime field in this case is now inside the dotted line of Fig. 5. If this was the true situation in the rocks we would pass out of the analcime stability field at depths much smaller than observed in nature.

Thus the combined study of the mineralogy and structure of the rocks and the study of one phase diagram leads us to the conclusion that in this part of the crust, the thermal gradient was about $20°$ km^{-1} and that fluid pressures were about the same as load pressures. More recent studies of other reactions tend to confirm these conclusions. In section 7 of this discussion we shall see another