Phase changes in the earth's crust—the record of crustal geophysics

W. S. Fyfe

The chemical and structural features of minerals preserve parts of the record of geological events: age, T *and* P *of formation, thermal gradients, magnetic field, etc. The correct use of such mineral memory units requires an exact knowledge of the possible equilibrium states of minerals in rocks and the kinetics of attainment of such states.*

1. Introduction

Geologists spend most of their time describing things on the surface of the earth. Occasionally they obtain a tiny view of deeper events by drilling holes and sinking mine shafts, but these rarely exceed a few kilometres in depth. What do they describe? In general the most important things include: the minerals present in a rock, the chemistry of the rocks and minerals and their fabric; the structure of the rocks, the geometrical arrangement of recognizable layers (faults, folds, etc.), the orientation of mineral grains, slip surfaces, etc.; the organic features of rocks (fossils, coal beds, organic debris). All these bits and pieces go together to form a geologic map which should tell what you will find at point X on the surface, and, if the structure is simple and topography cooperative, often a good idea of what may be encountered at depth. The geologist then continues by trying to reconstruct the history of the given part of the earth's crust. What I would like to try and show in this essay is how modern techniques may assist in the final analysis. It is an unfortunate fact of geological life that the parts of the earth we ever see form only a thin film making up no more than about 0·2 per cent of the total mass of the system. We want to know how the entire system works and to do this we must extract every possible drop of information from the processes we observe in this film. The scale of our problem is vast and the type and detail of information we may seek will be highly variable depending on whether we are collecting information about continental drift or the formation of gold deposits.

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2. Minerals have a memory

When we want to understand the dynamics of the crust the following types of question arise. When did this event happen? At what depth did this deposit form? How hot was the crust at 40 km when these rocks melted? Was the thermal gradient in the crust the same 4×10^9 years ago as it is today? How can we begin to answer such questions? It rapidly becomes apparent that if the information can be obtained, a memory of events must be frozen into the rocks themselves and their constituent minerals. There are some obvious examples.

Radiometric dating is now well known. Reactions involving radioactive decay are used in answering almost all questions about when and how fast. For example, a very common mineral in rocks is potash feldspar, $KAlSi_3O_8$. Natural potassium is a mixture of the three isotopes ^{39}K, ^{40}K and ^{41}K. The proportion of the isotopes is nearly constant in crustal materials. The isotope ^{40}K decays to argon (^{40}A) by electron capture and the half life 1.3×10^9 years is appropriate for geological dating. If we examine an old crystal of $KAlSi_3O_8$, it will contain a small quantity of ^{40}A and if this can be accurately measured and if we know that leakage from the crystal has been zero since its time of formation, we can date the growth of the crystal. Clearly, what is dated is a time relative to the assumption of zero argon loss. We know that feldspars leak rapidly at high temperatures so in fact we date the last rather cool event in the history of that crystal. If we date another potassium-bearing mineral in the rock with different diffusion characteristics we may get a different age, timing a different thermal or chemical event. Thus even with the simple dating process, interpretation is required. But at the same time, once the parameters of the processes are known a single rock may allow the timing of more than one event. In this case as in many others, we need to understand the conditions under which the mineral has a good or a faulty memory.

Today there is convincing evidence that the polarity of the earth's magnetic field has reversed many times during earth history. Studies of paleomagnetism have provided important evidence relating to such processes as continental drift and ocean floor spreading. Again, the record of the earth's magnetic field is locked up in the spin orientation of paramagnetic ions (Fe^{++}, Fe^{+++}) in minerals such as magnetite (Fe_3O_4). Again, the memory unit is temperature dependent and will only act at temperatures below the Curie or Néel temperature of the material. We must know that the mineral is chemically stable for if recrystallization occurs, the memory may be fuzzy. Techniques are available sometimes to clarify the memory by eliminating the weak components.

There are many ways by which temperature memories may be left in a mineral. Let us imagine that we are growing crystals in hot liquid water (note that the critical temperature of water is 374°C). When most crystals grow, they contain some holes filled with liquid. When we examine the crystal at low temperatures,

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we see the fluid inclusion or a cavity with liquid and vapour space. If we were to carefully reheat the crystal, we could observe the point where the vapour space vanishes. This may be a good measure of the growth temperature. We have cheated a little for we assumed liquid water and hence the pressure, but even this can be allowed for to some extent. Often too in natural crystals these tiny fluid inclusions may provide significant clues regarding the chemistry of the fluid in which growth occurred. And again, we must have evidence showing that leakage (in or out) did not occur.

Many other reactions in solids may give some information regarding temperature of formation. In the common feldspar minerals ($NaAlSi_3O_8$, $KAlSi_3O_8$, $CaAl_2Si_2O_8$) the Al–Si–O atoms form a continuous three-dimensional framework the charge of which is neutralized by the remaining cations which sit in rather large cavities in the framework. The Al and Si atoms are surrounded by four oxygens in a roughly tetrahedral configuration and are to a first approximation, equivalent structurally. At temperatures over 1000°C, these Al–Si atoms are randomly distributed in the structure. At lower temperatures they become ordered and occupy preferred sites. Such an order–disorder process is mainly sensitive to temperature. If a crystal grows at a certain temperature and is rather rapidly cooled, it may preserve a degree of order appropriate to the high temperature. Again, the memory is rate controlled. It is interesting to note that if we grow feldspars in the laboratory at low temperatures, and if we grow them rapidly, it is often the random feldspar we produce. The atoms are fixed in the growing crystal randomly because they arrive randomly. Clearly great caution is needed in using any such approach.

Today we have some rather new and more reliable methods of measuring some mineral temperatures. Natural oxygen is dominated by ^{16}O but contains a significant amount of ^{18}O. As the atomic weight of oxygen is rather low, fractionation tends to occur in natural processes. Thus the ratio of $^{16}O/^{18}O$ differs in snow–river water–ocean water, etc. It is also different in different minerals in the same rock. Any such isotope fractionation tends to be most efficient and hence most easily measured if the process occurs at low temperatures. For oxygen in minerals, considerable sensitivity is possible over most temperatures encountered in the crust. If a rock contains minerals such as quartz, alkali feldspar, calcite, or muscovite (all very common minerals), then fractionation between pairs such as quartz–calcite or quartz–muscovite, can provide a rather good measurement of temperature.[1] This type of thermometer can be calibrated by experimental studies. The measured temperature corresponds to a temperature below which exchange between phases is trivial. It is again a diffusion controlled and hence temperature sensitive memory. As far as is known reactions of this type are not sensitive to the pressures which would be involved in crustal processes. Oxygen isotope temperatures were first used to indicate the temperature of ancient seas by studying the $^{18}O/^{16}O$ content of carbonate fossils.

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So far, we have reached a point where, given a rock containing rather common minerals, we can say at what time and temperature it formed. What of pressure? This problem can be approached in many ways. Most common mineral species undergo phase changes in response to changing pressure and temperature. A compound A may thus change to a new structural state B by increasing pressure. The phase diagram for the two common forms of $CaCO_3$, calcite and aragonite, is shown in Fig. 1. Aragonite is denser than calcite and is stable at elevated pressures. Thus, if we see aragonite in a rock, it may have formed above the line X–Y in Fig. 1. This is a limit only, but if more than one such change is possible in the phases present in a rock, the limits become more narrow.

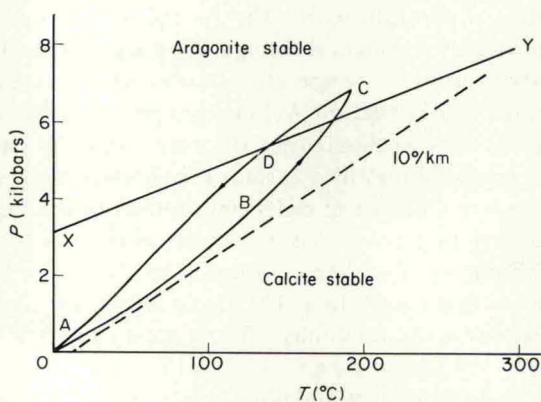This method of setting a pressure limit is full of snags. The phase diagram of

Fig. 1. Phase diagram for the system $CaCO_3$ showing stability regions of the polymorphs aragonite and calcite. Line X–Y represents equilibrium. A *P–T* line for a crustal thermal gradient of 10°/km is shown dotted. For other details see text.

Fig. 1 indicates *P–T* regions where each state has the lowest free energy and is the most stable chemical species in the given system. It is a diagram of chemical equilibrium. But crystal growth is a rate-controlled process and how can we be sure that the aragonite we see in a rock grew above boundary X–Y? It is an awkward fact that marine organisms in the oceans precipitate both calcite and aragonite in their skeletons at low pressures. The aragonite is a metastable phase. Thus before we apply this line of argument, we must be sure that we understand all the factors involved in the rate processes leading to equilibrium. In the case of the aragonite–calcite pair, we know enough to say that if the precipitation could have taken place over a few tens of years, do not use as a barometer. But if the crystallization process occurred above 200°C and involved a million year process, use with caution! We shall return to this mineral later.

Setting limits only, is hardly satisfying. A second type of reaction may yield

more significant results. Minerals are notorious for being impure. Most minerals form part of solid-solution series. This is true for almost all common rock forming minerals except quartz. Let us imagine we have two minerals A and B which can form a complete range of solid solutions under appropriate conditions. Let us further consider the case where A is a high pressure mineral while B is quite stable at low pressures. Mineral B forms C at low pressures. The phase diagram for the system A–B at a constant temperature will then appear as in Fig. 2. There is a field where only the solid solution is present and another field where a solid solution of given composition coexists with C. If in a rock we find a mixture of solid solution $+C$, then if we can find the temperature of formation (say by oxygen isotopes) we can say that for composition of solution x to coexist with C,
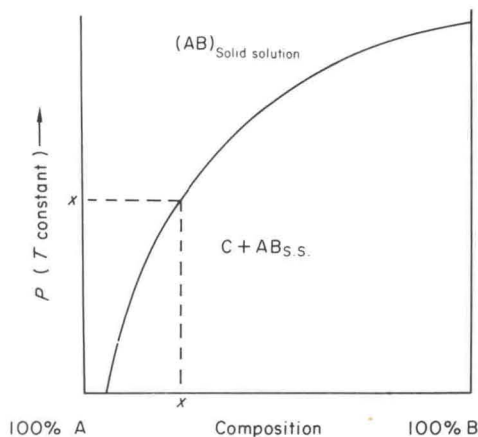

Fig. 2. Phase relations in a system A–B where A and B form one solid solution at high pressures but B is unstable at low pressures. At pressure x, the solid solution coexisting with C has composition x. The diagram is drawn for constant temperature.

the pressure must be P_x. The pressure is unique for a given temperature if chemical equilibrium is attained. Such equilibria abound in rocks and now we are beginning to use such solid-solutions to trace pressure history; in most cases this is equivalent to tracing the history of depth below the surface.

Many minerals which are members of solid-solution series, when examined chemically (as by the electron micro-probe) are found to be chemically zoned. The content of A and B will change from core to rim. The appearance of zoning indicates the very sluggish kinetics of diffusion of atomic species in many minerals. If this is the case, it is even possible that a single zoned crystal can more or less continuously record P–T events during its growth. Some day, we may have instruments for measuring the isotopic zoning as well as the chemical zoning.

It is very clear from the discussion above, that the mineral memory depends

on an equilibrium process which is assumed to occur at some stage and the freezing in of this information. Interpretation thus depends on knowing the significant equilibrium states and knowing how fast these states may change. History shows that workers tend to ignore the rate factors until anomalies accumulate to such an extent that a more cautious approach becomes essential.

Most equilibrium states are achieved more rapidly in response to rising temperatures than the reverse process in response to cooling. It is this fact that saves the day. Moreover, as we shall see below, certain catalysts tend to be more active when we heat rocks than when we cool rocks. The most important catalyst is water in the liquid or vapour state.

Certain information on processes can also be obtained from minerals. Consider that we find a quartz vein with a small amount of gold. We may wish to know how this material was transported into the vein. In general, we would expect aqueous solutions to have been active for we know that quartz is quite soluble in hot water. The oxygen isotopes of water from various sources are rather characteristic. Thus gases flowing from a very hot volcanic source would differ from those resulting from deep circulating surface water. If we know the temperature of formation of the vein system, and the fractionation coefficients of O^{16}/O^{18} between quartz and water, we may be able to say something about the source of the water and the quantities of water involved in the process. Understanding how geochemical processes occur is one of the most important aspects of economic geology.

3. The metamorphic cycle

In many active parts of the crust of the earth a very important series of events tends to be repeated, time after time. Continental rocks are eroded and transported to the oceans as sediments. As the sediment pile thickens, the sediments are depressed. As the sediments are depressed they go through a series of chemical processes and become metamorphic rocks. If the process continues long enough, the lower levels may become hot enough for melting to commence and igneous rocks are formed. These same igneous rocks may form parts of new mountain ranges which in turn become eroded to continue the process. Most geologists now believe that convective forces in the underlying mantle drive these spectacular processes. The margins of some continents are the situations where today we see these processes in operation. A complete cycle involves a time span of the order of 10^8 or more years. Understanding the cycle in modern situations and in older, now stable regions of the crust where remnants of past activity are to be found, is one of the most important aspects of all geological research. These processes record the thermal, dynamic and geochemical history of the earth, of the crust and mantle.

Let us look in a little detail at the materials and reactions involved in this

process. The sediments deposited near the continental margins accumulate in great basins known as geosynclines. Much of the debris has been transported by water and has reacted with water and the atmosphere. Some is sandy material consisting of mineral grains relatively little changed by surface reactions. Minerals, such as quartz, and feldspars may make up much of such sands. More muddy materials may have a much larger contribution from materials produced by surface chemical reactions; minerals such as clays, chlorites, zeolites, etc. These minerals are characterized by very large water contents; they are among the most highly hydrated minerals known. At times, massive contributions to the sediment may arise from the accumulation of skeletal debris of living organisms. Thus in appropriate situations massive deposits of calcite and aragonite (both $CaCO_3$) may form. The importance of such activity of the oceanic biomass can be appreciated when one considers some parts of the European Alps where mountain ranges are dominated by this material. At other times deposits of amorphous silica result from the accumulation of radiolarian skeletons. These rocks are termed cherts. The same debris may also form parts of more normal muds. In some thick geosynclinal deposits such as those of the New Zealand Alps or the Coast Ranges of California, much of the debris is derived from volcanic activity. It consists of volcanic mineral grains mixed with minor amounts of weathered materials and carbonates. Not infrequently, submarine lavas may make a significant contribution. These can often be recognized by their so-called 'pillow structure'. These same lumpy pillows have been photographed at modern volcanic centres in the Pacific Ocean, often in quite deep water.

Thus the primary sediment is a grand mixture of just about everything that can resist weathering and be washed off the continent, everything that can form by weathering and all the things that organisms secrete. It is wet both because of chemically bound water and because of a high porosity. It is reactive, because it contains so many fine particles and even amorphous materials.

As this material is covered and buried the first process to occur involves the reduction in porosity. At the surface pore volume may be as large as 40 per cent but by the time burial reaches 2 km this is reduced to 1–2 per cent. At 5 km depth, it is vanishingly small. Porosity will be in part removed by purely mechanical processes and in part by more soluble materials dissolving at site of stress concentration and reprecipitating in stress shadows. By the time the rock reaches this 5 km burial, most of the water will be bound in hydrated minerals. Many of the main sedimentary minerals will still be rather stable but some more reactive materials may have been reorganized.

As the sediments sink they will also be heated by the normal heat flow coming from the interior of the earth. Unless the rate of accumulation is catastrophically fast they will reach thermal equilibrium almost as fast as they sink. Heat flow and conductivity measurements show that temperatures will rise by something

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like 10–30°/km. By the time 5 km burial is achieved, temperatures will be of the order of 100°C. A few reactions that might be expected to proceed even under these mild conditions would include:

metastable aragonite →calcite
amorphous silica →fine quartz
amorphous clay materials→crystalline clays and chlorites
very fine crystals →larger crystals

By the time these processes have occurred, the muddy sediment has become a rock.

Even at quite moderate temperatures some of the hydrated minerals may proceed to dehydrate. Normally these dehydration reactions can be envisaged to proceed in steps:

$$X . n \, H_2O \rightarrow X \, (n-1) \, H_2O \rightarrow X(n-2) \, H_2O \text{ etc.}$$
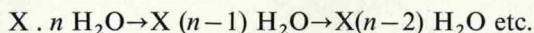
With most familiar chemical hydrates these steps are distinct and lead to a regular pattern of vapour–pressure curves (Fig. 3). But when extensive solid
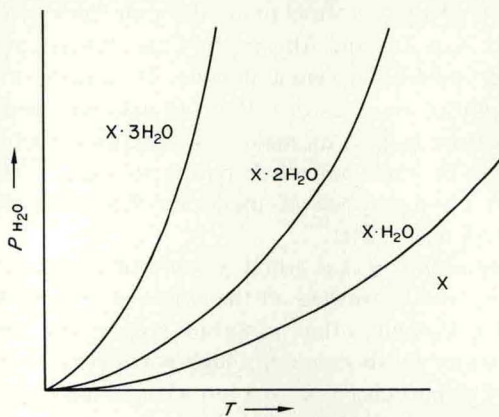
Fig. 3. The normal form of vapour pressure curves for a series of hydrates at low pressures.

solutions are involved as with clay minerals and chlorites, one may expect a more or less continuous dehydration reaction.

If porosity is large, water may flow out via a continuous pore system. If this occurs, the water pressure will be about that corresponding to a water column of appropriate height. The pressure on the solid phases will be greater for these must bear the load of sediment. Thus to a first approximation, in the upper levels, $P_{H_2O} \simeq \frac{1}{3} P_{rock}$.

As sinking continues, porosity and permeability begin to decline to very small values. Heating and water evolution continue but the released fluid has a more difficult task fighting its way to the surface. Measurements in deep bores have

shown that after about 5 km, the fluid pressures begin to approach the rock pressure; the escaping fluids are almost lifting the rocks to escape. It is interesting to note that this effect may play a large part in the formation of enormous gravity slides where mountain-sized blocks of rock slide at very low angles. Friction is reduced by high-pressure gas lubrication. There is a considerable body of evidence to suggest that when wet sediments are deeply buried and progressively dehydrated, fluid pressures are about equal to (or possibly slightly exceed at some places) the total overburden or lithostatic pressure. Chemical reactions may thus proceed in a wet environment where water pressures and temperature are both simple functions of depth.

In principle the reactions are simple; in detail often very complex on account of the complex chemistry of the average rock. Examples of some simple reactions are:

$$\text{quartz} + \text{clay} \rightarrow \text{pyrophyllite} \rightarrow \text{silicate}$$
$$2SiO_2 + Al_2Si_2O_5(OH)_4 \rightarrow Al_2Si_4O_{10}(OH)_2 + H_2O \rightarrow Al_2SiO_5 + 3SiO_2 + H_2O$$
$$\text{zeolite} \rightarrow \text{feldspar}$$
$$SiO_2 + NaAlSi_2O_6 \cdot H_2O \rightarrow NaAlSi_3O_8 + H_2O$$
$$\text{clay} + \text{feldspar} \rightarrow \text{mica} \rightarrow \text{silicates}$$
$$Al_2Si_2O_5(OH)_4 + 2KAlSi_3O_8 \rightarrow 2KAl_2Si_4O_{10}(OH)_2 + H_2O \rightarrow 2KAlSi_3O_8$$
$$+ Al_2SiO_5 + SiO_2 + H_2O$$

At rather high temperatures, carbonates may begin to lose CO_2 and become silicates:

$$\text{calcite} + \text{quartz} \rightarrow \text{wollastonite} + CO_2$$
$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$$

The low temperature assemblages of sediments are dominated by zeolites–clays–chlorites–silica–carbonates; at moderate temperatures micas–feldspars–epidotes–chlorites–quartz become dominant and at the highest temperatures when little water remains minerals such as feldspar–amphiboles–biotites–garnet begin to dominate the mineralogy. The $P-T$ conditions for most of these dehydration reactions are approximately known from laboratory studies.

By the time we reach the highest grades of metamorphism the original mud which perhaps contained 20 per cent H_2O, will contain only 1 or 2 per cent. If burial or depression by convective forces is extreme, these slightly wet rocks may begin to melt. The rock now becomes a mixture of an aqueous silicate melt and a very dry residue. The melt is called magma and when we see a rock which shows the mixture we call it a migmatite. Such regions of the crust are often seen in the eroded roots of old mountain regions.

Rocks which are wet or partly wet melt at much lower temperatures than dry rocks. Consider a system $A-H_2O$, where a hydrate, $A \cdot H_2O$ of great thermal stability is formed. The melting relations of A will normally be as in Fig. 4(a). Pressure increases most melting points. If a large amount of water is present,

enough to saturate the melt at all times, the melting in the wet system will appear as in Fig. 4(b). If the vapour–pressure curve of the hydrate intersects the melting curve as shown in Fig. 4(b), then the system A . H_2O (no excess water) will melt as in Fig. 4(c). These curves, intermediate between the totally dry and wet curves, are those that are most likely to be significant if melting occurs near the base of the earth's crust.

Experiment shows that the first fractions of melt likely to be formed by this process have a composition similar to rhyolites which occur as surface volcanic rocks and granites which form huge intrusive bodies of igneous rocks invading various crustal levels. The accumulation of this liquid into huge drops which rise, is possibly related to the viscosity contrast between a partially molten zone and unmelted cooler crust. Small drops of light liquid can rise rather rapidly in
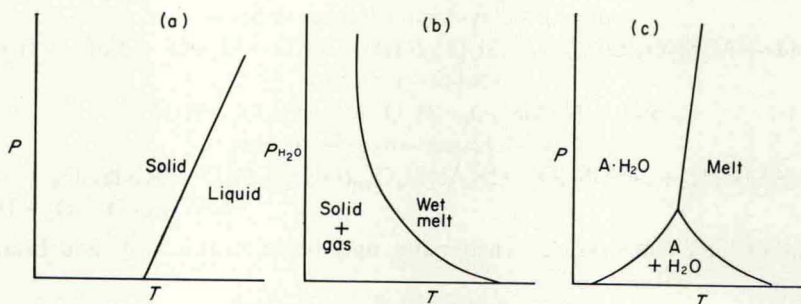
Fig. 4. Melting relations in a system A with and without water. (a) The dry system. (b) The system with excess water, $P = P_{H_2O}$. (c) The system when water is contained only in a hydrate A . H_2O where the vapour–pressure curve of the hydrate intersects the depression of freezing curve.

the hot zone but will slow down in the cool zone. If we apply Stoke's law to such a problem we see why only large drops can invade the viscous solid crust.

As soon as partial melting commences dehydration reactions now proceed via the general process:

hydrated minerals + anhydrous minerals
↓
melt + less hydrated residue
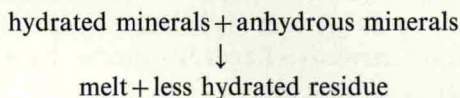
The water of dehydration now rises to the surface as part of a fluid phase dominated by silicate liquid. While the condition

$$P_{fluid} \simeq P_{Lithostatic}$$

may still apply, it must be remembered that P_{H_2O} is only a part of P_{fluid} possibly a part as small as 10 per cent. Thus in the migmatite zones we must consider dehydration reactions where the solids are under greater pressure than the

water pressure in the environment. This situation leads to dehydration at lower temperatures than might be expected.

The residue of partial melting is enriched in Fe–Mg minerals. Pyroxenes and some very stable amphiboles, garnets and other anhydrous materials are common. Rocks of this type are often called granulites and are common in the root zones of old parts of the crust, particularly in Pre-Cambrian shield areas.

4. Prograde and retrograde processes

In part two of this paper we discussed mineral memories and emphasized how important it is to understand when the memory begins to function. In the section above we have suggested, that when rocks are heated and undergo prograde metamorphism, they tend to attain equilibrium states. This is hardly surprising for if we can study comparable reactions in the laboratory (almost always under very wet conditions) then clearly as geological times exceed laboratory times by factors of 10^7–10^8, then reactions should reach equilibrium. But just as rocks are slowly buried, they are slowly uncovered. Why then are the reactions not reversed?

There are two main cases to be considered, those involving wet and dry reactions. In the case of wet reactions it is clear that as the necessary water is lost during the heating cycle, to reverse the reactions it must be replaced at appropriate temperatures. Metamorphism reduces porosity and permeability. There is good evidence that it is much easier for the water to leave (virtually by splitting the rock open) than to return. Certainly, trivial amounts of back reaction can be found in most rocks, but it is trivial because first the water is not available and second, its rates of diffusion into the high grade rock is very slow.

When we consider the second class of reactions involving dry solids and including the numerous cases of polymorphism, these solid-state reactions are very slow because they involve movement of atoms or ions in the solid state. The reactions have very large energies of activation which control the rates of reaction. Equilibrium is much more likely to be attained in response to a rising than to a falling temperature. This type of process can be easily studied in a laboratory and reversibility is normally never achieved if the heating and cooling cycles are of comparable duration. However, an even more important consideration in these reactions is again the presence of an aqueous fluid. Many solid–solid reactions would not occur even in geologic times unless a solvent is present to promote material transport. Most inorganic oxides have quite appreciable solubilities in water at elevated pressures and temperatures. Thus the prograde reaction proceeds when a fluid is present but it does not reverse unless the fluid is still present during cooling. This is generally not the case. Doubtless, there are changes which do reverse, some we are well aware of (e.g. the α–β quartz transition), others we may never be aware of for in many ways the rocks themselves

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guide our thinking on what to study. Some reactions are not reversed except under special conditions and hence point to these same special conditions in nature (see calcite–aragonite below).

5. The controlling variables

Once we have seen rocks and their minerals and the reactions which occur, before we commence laboratory studies we can list some of the variables which must be considered. The crust of the earth rarely exceeds 50 km in thickness; this means that lithostatic or load pressures must rarely exceed 15 kb. Thermal gradients are variable. We know that in some regions some rocks melt at depth, a reaction requiring temperatures of perhaps 1000°C. This is unusual and implies that thermal gradients as high as 20–30°C/km must also be unusual, otherwise most crustal masses would be partly molten at the base all the time. We also know that some common rock types probably never melt in the crust and this confirms our upper limit.

On any long-term basis, the crust is not very strong. It is better considered as a very viscous fluid, with a viscosity exceeding 10^{20} poises. Birch[2] considers that long-term stresses probably rarely exceed 10^2–10^3 bars. They are thus not important relative to load except in very special places such as in an active fault zone. Stress can have important effects in increasing reaction rates in solids but these small natural stresses will not shift equilibrium states drastically. The parameters P–T–P_{stress} define the chemical potentials or free energies of the mineral species in a rock. We normally ignore the stress contribution. Time will tell if this is always justified.

When a gas phase is involved, we need to know the total gas or fluid pressure and the partial pressures of all the species in the gas. So far we have been mainly concerned with pure water but in most rocks we will have partly saline solutions and contributions from other species such as CO_2, O_2, H_2S, HF, etc. Water, CO_2 and salts are by far the most dominant solution species in most cases.

Today, we have apparatus which will allow us to do limited types of experiments over all this crustal range and in some cases much more than this. Shock wave experiments can even produce pressures greater than 10^6 bars, pressures which are encountered at the centre of the earth. We can study phase changes, measure solubilities, reaction rates, etc. There are many measurements we would like to make which are difficult, for example most types of absorption spectrometry. At high P and T in the presence of water, there are few materials not subject to corrosion. But as the need arises, these problems tend to be solved and our knowledge of the physical chemistry of the crust is slowly being extended.

6. Some examples of significant mineralogical reactions

6.1. *Equilibrium between analcime, quartz and albite*

In 1954, Coombs[3] described the mineralogical changes in a very thick pile of

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:

$$\text{analcime} + \text{quartz} \rightarrow \text{albite} + H_2O$$
$$NaAlSi_2O_6 \cdot H_2O + SiO_2 \rightarrow NaAlSi_3O_8 + H_2O$$
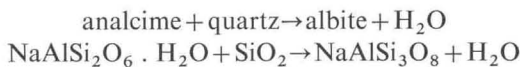
Obviously, if we knew the conditions of this reaction exactly, we would also know something about water pressure and temperature in the environment.

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 thermodynamics 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 equilibrium. 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 $\simeq 4.5$ 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.
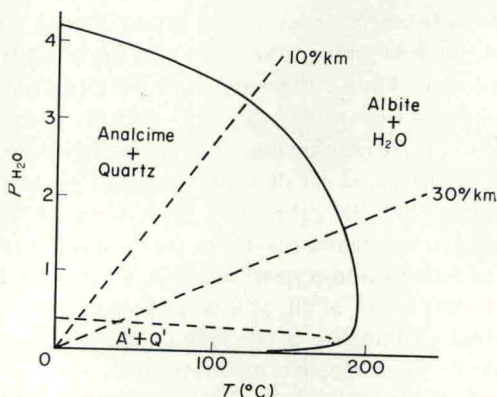
Fig. 5. Stability field of analcime + quartz. The full line corresponds to condition, $P_{H_2O} = P_{Total}$. The dashed line indicates the approximate reduction of this field when $P_{H_2O} \simeq \frac{1}{3} P_{Total}$. Geothermal gradients of $10°$ and $30°$/km are indicated.

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

study of a thick sedimentary pile where the geothermal gradient is much lower. Given these types of data we can begin asking the big question: why?

6.2. *Equilibrium between the polymorphs of Al_2SiO_5*

When clay rich sediments are heated to moderate temperatures, three forms of Al_2SiO_5 commonly appear. These are the minerals kyanite, sillimanite and andalusite. Geologists could tell us that kyanite seems characteristic of deep environments and sillimanite of hot environments. Can we find the exact conditions of these reactions? At first sight the problem looks simple because these are supposed to be compounds of identical chemical composition.

Entropy and volume data are available for the three substances. Thus we know that

$$S_{Sillimanite} > S_{Andalusite} > S_{Kyanite}$$
$$V_A > V_S > U_K.$$

The slope of a phase boundary between two polymorphs is given by the relation

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

and hence with these facts alone we can say that the phase diagram must look like Fig. 6. It remains to find where the lines lie in space.
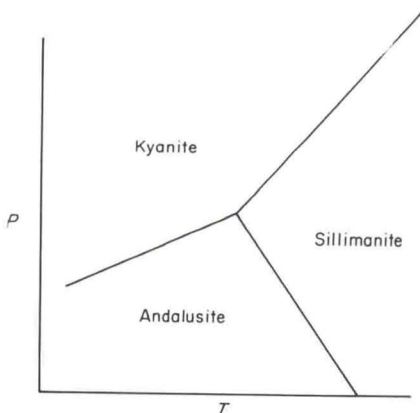
Fig. 6. Form of phase diagram for the three polymorphs of Al_2SiO_5 necessitated by entropy and volume data.

When we examine the values of entropy changes and relate these to chemical affinities through the relation

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S$$

where ΔG is the change in free energy, we again see that we are dealing with

trivial chemical affinities. In fact, for the andalusite–sillimanite reaction, ΔS is almost zero over a large range of temperatures.

Today, we know a little about this phase diagram, and the cost of obtaining the data probably exceeds a million dollars. Many methods of study have been tried and many were obviously useless even before they were tried. Geology tells us that these are very slow reactions for often a single rock contains two or even three forms together one or two of which must be unstable.

At very high temperatures, mixtures of A and K and S and K will react at measurable rates and hence a good fix on the boundaries is possible. Reactions
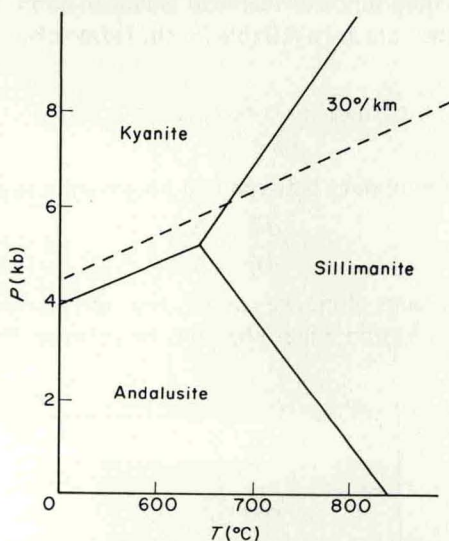
Fig. 7. Experimental phase diagram for Al_2SiO_5 polymorphs. While the boundary between kyanite and sillimanite is rather well determined, that between andalusite and sillimanite is not well known.

between A and S have not yet been shown convincingly. Another profitable approach has been used. If kinetics of growth and nucleation are slow, we can make use of the much faster rates of solution to find equilibrium. If we dissolve two polymorphs in the same solvent under identical P–T conditions, and if an equilibrium solubility can be measured, then we know that if

Solubility of A > Solubility of B

then free energy of A > free energy of B.

We can find points of equilibrium ($G_A = G_B$) by this technique.

Weill[5] used this technique and chose the very excellent solvent, fused cryolite, Na_3AlF_6.

If we use the available data, the phase diagram must be about as in Fig. 7.

If the diagram is correct and at least the A–K and S–K lines seem fairly well established, then clearly if a rock contains or is dominated by one polymorph, we can place that rock in a P–T region appropriate to the diagram. We can tell much more if we have clues about the depth or temperature.

If we place geothermal gradients on Fig. 7 some perhaps surprising results appear. It is clear that if the thermal-gradient is not of the order of $30° \text{ km}^{-1}$ or greater, then all metamorphic rocks would contain kyanite only. Andalusite is only common where hot silicate liquids invade the higher levels of the crust so it presents no problem. But kyanite–sillimanite transitions are not uncommon in progressive metamorphism which suggest that these steep thermal gradients frequently occur. This brings us to a most important conclusion once stated by Fyfe, Turner & Verhoogen[6] 'that heat must be introduced at a rate greater than normal to account for the development of high-grade metamorphic rocks at
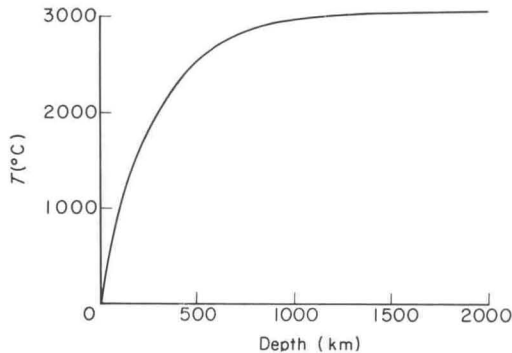

Fig. 8. A possible thermal gradient in the mantle. Many models are possible for such gradients, none are certain.

reasonable depths'. This statement is even more obvious if we consider the thermal gradient in the entire earth (Fig. 8). The gradient over the first 100 km averages no more than $10° \text{ km}^{-1}$. We do not yet understand this thermal problem but I was most interested in a suggestion made by Professor M. Bott of Durham University that part of the heat source could be due to frictional forces related to convective motion in the upper mantle. Certainly, mantle convection is connected with the dynamics of metamorphism and mountain building. The point I wish to stress here is that experimental studies allow us to put some numbers on the problem and allow us to determine the exact pattern of anomalies over a vast range of geological time.

6.3. *Calcite–aragonite*

The two minerals calcite and aragonite are polymorphic modifications of $CaCO_3$. They both occur commonly in sedimentary rocks and in some meta-

morphic rocks. The phase relations between them are rather well established both by direct studies of the transition and by the indirect solubility approach. The phase relations are shown in Fig. 1. At normal surface temperatures calcite is the stable phase and a pressure of 3–4 kb is required to stabilize aragonite. These pressures would correspond to a depth of burial of about 11 km. In general the polymorphs occur in the pure state and impurities are not likely to significantly change the phase relations.

If we consider places where the polymorphs occur, it is apparent that the formation of these carbonates does not always follow an equilibrium pattern. Marine organisms often secrete a calcareous skeleton and often this is made of both calcite and aragonite. The marine muds derived from this organic debris also contain both species. If we examine older calcareous muds, aragonite becomes rare but in exceptional cases, aragonite skeletons are preserved for hundreds of millions of years. In some hydrothermal regions, particularly those near ultrabasic rocks, both polymorphs may be crystallized from spring waters near the surface. If we examine all high temperature metamorphic rocks, these contain only calcite. Aragonite is found in only one class of metamorphic rock, glaucophane schists, which contain a large number of other high pressure phases (see below).

It is obvious from Fig. 1 that when aragonite occurs in a low pressure environment it does so as a metastable phase. As such it should be subject to alteration to more stable calcite. The kinetics of this low pressure reaction in aqueous solution has been studied for at least a century for these two minerals provided the first example of mineral polymorphism recognized in 1788.

We may note a few general features regarding the growth of aragonite and its conversion to calcite. Aragonite will nucleate from a supersaturated solution in preference to stable calcite:

(1) when the temperature is near 100°C
(2) when the solution contains appreciable quantities of ions such as Mg^{++}, Sr^{++}, SO_4^{--}, and many others in solution.

The rate of transformation to calcite is greatest when:

(1) solutions have a large salt concentration
(2) when the partial pressure of CO_2 is high
(3) at high temperatures
(4) when Ca^{++} is large.

The reaction is inhibited by:

(1) ions like Mg^{++}, Sr^{++}, OH^-
(2) hydrophobic materials adhering to the aragonite.

When metastable aragonite persists in nature it is generally for one of three

reasons; high Mg^{++} (as in the oceans), hydrophobic organic coatings as with fossils or an anhydrous environment (as in some metamorphic rocks). Studies of the reaction rate have clearly shown that in wet environments, metastable aragonite could not persist for the normal times of a metamorphic or sedimentary cycle. This is well borne out by observations on buried sediments.

The aragonite–calcite transformation is even quite rapid in the solid state at moderate temperatures. At one atmosphere and about 400°C, the transition takes only minutes or hours to occur. But at 200°C and 1 atmosphere pressure, the time would be of the order of millions of years. Thus in a dry low temperature environment, aragonite, if formed, can survive.

If we study some of the sediments on the West Coast of the United States we find that as they become progressively metamorphosed, calcite is converted to aragonite. If we examine Fig. 1 it will be noted that only very low thermal gradients will allow this transformation. Now let us imagine that burial has followed a path such as A–B–C. During this burial water will be progressively eliminated and at early stages the metastable aragonite would change to calcite and then later, near C, aragonite forms as a stable phase. Now the rocks are unloaded and return to the surface along some path C–D–A and the aragonite survives for us to observe it. Clearly, if we knew all about reaction rates, we could limit possible paths. First, we can say that along the path C–D–A, fluid phases must be absent for if this was not the case, it is impossible to see how the aragonite could survive once in the field of calcite. Second, the higher the thermal gradient, the longer time aragonite will pass through the calcite field and the higher the temperature at which it will enter the calcite field. From studies of the kinetics of the solid state reaction, both temperature and pressure coefficient, it is possible to say that unless the aragonite re-enters the field of calcite stability at about 200°C or below, then survival is most improbable. This suggests that the thermal gradient during unloading must have been less than $10° \text{ km}^{-1}$. The reaction rates are so temperature sensitive (the activation energy is so large) that this result carries a very small uncertainty, possibly one or two degrees. We thus have an example of reaction rate parameters being used to limit geophysical parameters.

6.4. *Eclogites*

Basaltic rocks are the most common product of volcanism. It is now certain that basaltic liquids originate in the upper mantle at depths of the order of 100 km. When basalts are compressed, they can be transformed into a much denser rock called eclogite. Eclogites have always attracted the attention of geologists for a number of reasons. They are dense considering their chemical composition. They consist of only two minerals; a red garnet and a green pyroxene and can be most attractive in appearance. They have properties which make them appropriate as possible major components of the upper mantle of the earth.

Eclogites occur on the surface of the earth in a number of situations. Minor

inclusions are sometimes found in lavas and these could represent mantle fragments or products of very deep crystallization. Some are found as fragments in the kimberlites in which diamonds are found. These too, come from the mantle. They occur as lenses and bands in some areas of deeply eroded ancient crust and in some modern active tectonic belts on continental margins. Many workers have tended to consider eclogites as mantle products and if they are found in the crust have considered them introduced by some mechanical process. Other workers have shown that some eclogites are the product of metamorphism of basaltic lavas once on or near the surface of the earth. They have been buried deeply or dragged down by tectonic forces until they were transformed. They thus occur associated with rocks which reflect moderate (400–500°C) to very high temperatures (1200°C).
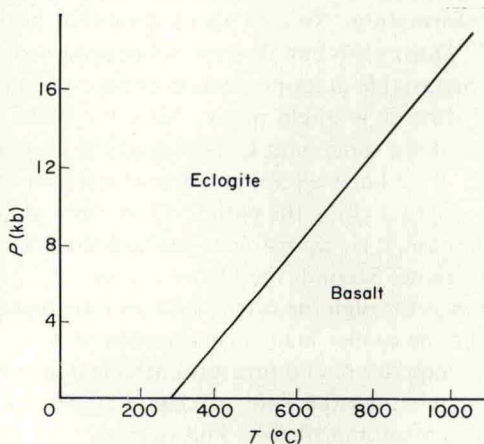

Fig. 9. Approximate position of equilibrium between basalts and eclogites. In reality, this line is a broad band of transition.

The eclogite–basalt transition has been studied experimentally by numerous workers. In Fig. 9 data from Green & Ringwood[7] is shown. If these data are reliable at low temperatures, it is clear that eclogites can form from dry basaltic materials in the crust. The problem of their formation would then be a problem of reaction rates in a dry medium. There are plenty of deeply buried basalts which have not been transformed.

Basaltic rocks when metamorphosed in the crust, generally become hydrated and form schists rich in hydrated minerals (chlorites–epidotes–amphiboles). These rocks fit the normal pattern of progressive metamorphism where $P_{H_2O} \simeq P_{Load}$. It has been suggested that just as analcime is dehydrated at high water-pressures (Fig. 5), these hydrated basaltic rocks could be transformed to dry eclogite, but at very high fluid pressures. Thus the phase relations in the wet

system would be as in Fig. 10(a). In terms of geological occurrence, there is much to commend this form of diagram.

As yet, while there is experimental data on curves A–B and B–C of this diagram, there have been no studies of curve B–D at low temperatures and there is every indication that the rates of reaction are very slow indeed. In part this is due to the complex chemistry of the system and the statistical difficulties of attaining an equilibrium state; many atoms must move in this transformation.

When a problem of this type is faced, time after time, simple thermodynamic arguments can help. With mineral reactions we almost always have data on
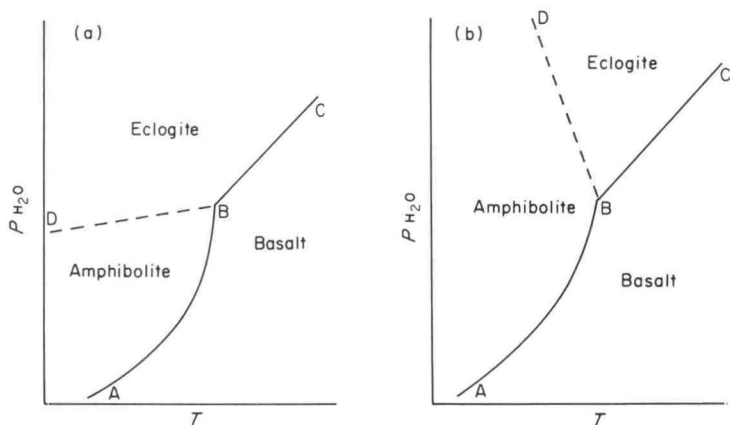

Fig. 10. Possible phase relations in the wet basalt system (ignoring regions of partial melting). (a) A diagram suggested by field occurrence. Eclogite could be stable in wet crust. (b) The most probable form demanded by thermodynamic arguments. Eclogite only stable in dry crust.

volume changes. We can thus use the relation

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V$$

if we can get some fix on ΔG at any one pressure. In the present case we have an equilibrium curve for reactions:

$$\text{hydrate} \rightarrow \text{basalt} + H_2O \tag{1}$$

and

$$\text{basalt} \rightarrow \text{eclogite} \tag{2}$$

and hence we have some points where ΔG's for (1) and (2) are zero. Because of the properties of the free energy function we can add ΔGs of (1) and (2) to get ΔGs for the reaction:

$$\text{hydrate} \rightarrow \text{eclogite} + H_2O$$

and as we know the ΔV terms, we can draw the phase diagram. If we do this,
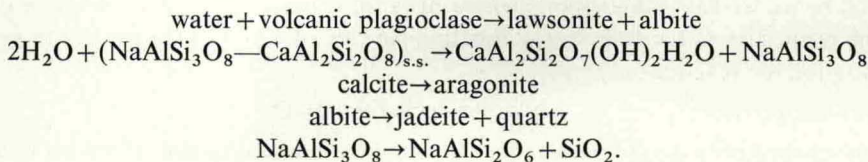
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we see that Fig. 10(a) cannot be correct and the true equilibrium diagram must be more like Fig. 10(b).

If this diagram is correct and if crystal rocks are metamorphosed to eclogites then water pressures must be much lower than load pressures. The products of metamorphism are totally different from those occurring in the more common wet conditions. Moreover when and how the reaction proceeds is rate-controlled and may seldom represent an equilibrium state. It seems possible that there may be many other cases of metamorphism, where aqueous phases have had only a limited influence. These factors must be recognized before we decide what significance should be attached to a given type of reaction in a given geological situation.

7. A case history—burial metamorphism on the Pacific margin

To conclude this essay, I would like to briefly mention some results from field and laboratory studies of the rather unique series of metamorphic rocks which are found scattered in large and small fragments around almost the entire Pacific margin. The rocks are all of similar age. Other comparable belts run through the Alps, Greek Islands, Turkey and Northern India, and another in the Urals. It is possible that some too, may have been obliterated by later events. While the characteristic minerals to be described are widespread in these narrow belts of global length, they are strikingly absent from other metamorphic rocks making up a much larger contribution to the metamorphic terranes of the earth's crust. These same belts are closely related to the modern seismic and volcanic zones of the earth. Some of the most active fault systems of the earth, with enormous lateral displacement, run through the belts. Today we recognize that these zones are in regions where ocean sediments are driven deep beneath the continental margins by convective forces which also drive the ocean floor spreading process.[8]

The rocks in these belts are dominated by volcanic debris. Thicknesses are unknown but considered in places to be of the order of 15 km. But if convective forces are at work, thickness should not be confused with burial for materials may be driven to much greater depths. Many of the rock types are little altered but in places there is widespread development of the characteristic minerals jadeite, lawsonite, aragonite, glaucophane. The first three can be considered to develop by the rather simple reactions which seem to occur in the following sequence:

$$water + volcanic\ plagioclase \rightarrow lawsonite + albite$$
$$2H_2O + (NaAlSi_3O_8\text{---}CaAl_2Si_2O_8)_{s.s.} \rightarrow CaAl_2Si_2O_7(OH)_2H_2O + NaAlSi_3O_8$$
$$calcite \rightarrow aragonite$$
$$albite \rightarrow jadeite + quartz$$
$$NaAlSi_3O_8 \rightarrow NaAlSi_2O_6 + SiO_2.$$

Each of these reactions has been studied in the laboratory and the relevant phase boundaries are shown in Fig. 11.

It will be noticed that the occurrence of lawsonite places an upper limit on the temperature of metamorphism at about 400°C. At low Ps and Ts a zeolite laumontite also restricts the lawsonite field. Further, we know that in complex chemical systems other phases tend to restrict this field even more so that a temperature limit of 300°C is likely to be nearer the truth. The subsequent reactions call for little comment, so burial along a gradient of about $10°$ km^{-1} to a depth of 30 km would explain the mineralogy. If these rocks are unique, so is the depth of burial and the low thermal gradient. It is also no surprise (cf. Fig. 8) that these rocks should be associated with eclogites; pressures are certainly high enough.
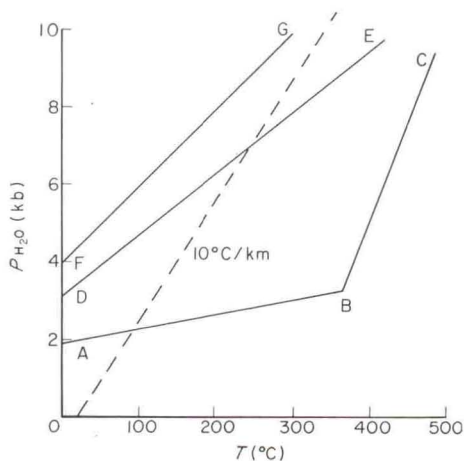

Fig. 11. Stability fields of minerals related to glaucophane schists. Lawsonite is only stable within the area bounded by A–B–C. Aragonite is stable above D–E. Jadeite with quartz is stable above F–G. A low geothermal gradient is shown.

Most other evidence points in the same direction. As already mentioned, the occurrence and preservation of aragonite indicates the same type of thermal gradient. Oxygen isotope fractionation gives temperatures of 250–300°C. The feldspars in these rocks show an extreme degree of order. There are still many unsolved problems and many aspects of the experimental data require confirmation, but one may doubt if refinement will greatly change the picture. It is now a problem for the geophysicist to explain the thermal regime.

If this type of metamorphism is related to descending convection currents in the upper mantle and to ocean-floor spreading, it is possible that remnants of it inside continental masses may point to the operation of ancient convective cells,

as in the Ural Mountain belt. In this way we may be able to unravel many aspects of the thermo-mechanical history of the earth.

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