

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 $30^{\circ} \text{ km}^{-1}$ 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 & Verhoogen⁶ 'that heat must be introduced at a rate greater than normal to account for the development of high-grade metamorphic rocks at

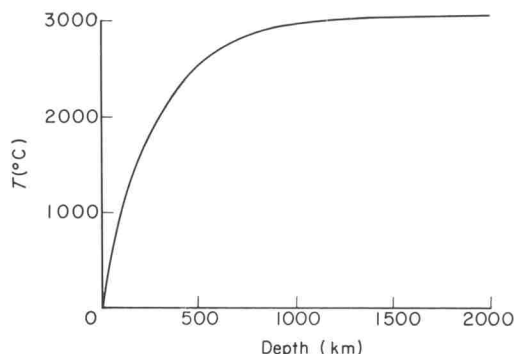


Fig. 8. A possible thermal gradient in the mantle. Many models are possible for such gradients, none are certain.

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 $10^{\circ} \text{ km}^{-1}$. 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-

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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