

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 ($\text{NaAlSi}_3\text{O}_8$, KAlSi_3O_8 , $\text{CaAl}_2\text{Si}_2\text{O}_8$) 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 $^{16}\text{O}/^{18}\text{O}$ 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 $^{18}\text{O}/^{16}\text{O}$ content of carbonate fossils.

Phase changes in the earth's crust

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

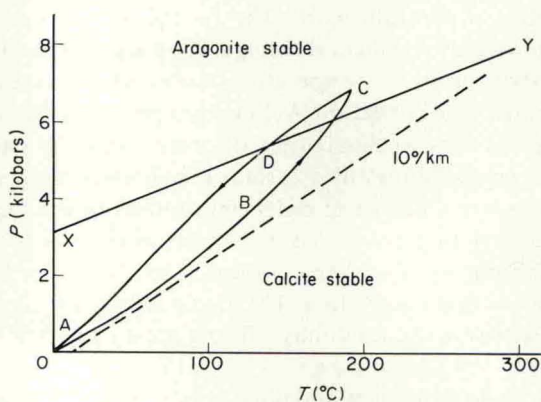


Fig. 1. Phase diagram for the system CaCO_3 showing stability regions of the polymorphs aragonite and calcite. Line X-Y represents equilibrium. A P-T line for a crustal thermal gradient of $10^\circ/\text{km}$ is shown dotted. For other details see text.

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