CONTEMPLATIONS ON CERTAIN TYPES OF METAMORPHIC REACTION

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ABSTRACT.

The great majority of metamorphic reactions take place in, and are aided by, the presence of water or some other fluid phase. This, however, may not always be so, and evidence is assembled to show that under conditions of high-grade metamorphism reactions could take place entirely in the solid state.

Although our knowledge of the conditions of formation of metamorphic rocks is today making great advances, it is still a matter in which there is a great deal of uncertainty. This is particularly striking when we make a comparison with available data on the origin of sediments and igneous rocks.

The actual formation of many sedimentary rocks can be studied by visual observation and the conditions measured with a great deal of accuracy. Where this is impossible, as in the oceanic abysses, methods which are only slightly less direct are available. Similarly the conditions for the solidification of igneous rocks seem to have become reasonably clear to us through the study, first, of simple systems of dry melts, and, more recently, of systems containing volatile components.

Conditions for the formation of metamorphic rocks, however, vary over an extremely wide range. Temperatures vary from as low, possibly, as 100°C. up to 700 or 800°C., pressures up to 15,000 or even 20,000 bars. The effect of directed pressure is controversial, and while the presence of water is known to be of great importance, it may sometimes be absent.

The fundamental feature of metamorphism is that the rocks remain essentially solid. But while this is so the presence of a fluid, which may be in extremely small quantity, is a most important factor. This is supported by theoretical considerations as well as by experimental work. It is obvious that water is much the most important of these fluids.

The great majority of metamorphic rocks provide their own evidence for the presence of potential fluids. The hydroxyl ion can be present in rocks of high metamorphic grade. As an example the (OH) in hornblende is present in amphibolites which persist up into the sillimanite zone of Barrow's classical locality in Scotland. It is only in the rare rocks conforming to the granulite, eclogite and pyroxene-hornfels facies that we have assemblages consisting entirely of anhydrous minerals.

However, we know that an anhydrous assemblage of minerals does not necessarily imply that the system was a dry one when the rock was formed. It does however suggest that we might question the correctness of the assumption that a solvent—generally water—must always be present. Therefore we should consider the possibility of reactions having taken place completely in the solid state.

REATIONS IN THE SOLID STATE.

Our knowledge of the chemistry of solids has recently advanced very rapidly and for this we thank technologists as well as the crystal chemists. Three properties possessed by the solids themselves greatly affect potential reactivity—grain-size, the shape of grains and the crystal structure. As reactions between
solids must begin and proceed from points of contact, the effects of grain-size and shape are obvious. Decrease in the grain-size increases the area of possible contact; also a platy mineral will present a greater area per unit volume than will a mineral which consists of spherical grains. A measure of these two factors is combined in one term, surface area per unit weight, of which great use is made in industry.

If we wish to bring about a reaction between two solids experimentally we therefore grind them as fine as possible and mix them thoroughly to ensure the maximum number of points of contact between the grains. This would be increased by compressing the mixture. It would then generally be necessary to raise the temperature before reaction proceeded at a significant speed.

The mechanism of reaction in its simplest form between two solids can be pictured firstly as the formation, at the area of contact, of a surface film of the reaction products (Cohn, 1948). This film formed by surface diffusion of the more mobile component would have a thickness of about one molecule and would not be in an orderly arrangement. It would thus not be detectable either by chemical analysis or by X-ray examination. This first interaction which involves only surface particles can take place at comparatively low temperature.

Further reaction depends on the reacting particles possessing enough energy to diffuse through the surface layer of reaction product into the interior of the lattices, and the molecules of the new compound being sufficiently mobile to arrange themselves in the ordered form of the new crystal lattice. Increase in temperature can, of course, supply both these requirements, but the amount of heat necessary may be greatly modified by the nature of the crystal lattice of the reacting substances.

In natural minerals, as well as in prepared solids, the stability of the crystal lattice must be a most important factor, i.e. whether the minerals are within their true stability ranges or are metastable under the conditions of metamorphism. As an extreme instance we can think of the instability of tridymite under most conditions of metamorphism. Quartz is the form of silica generally stable under such conditions. The instability of tridymite should make it enter readily into solid reactions. Another point concerns the openness of the crystal structure. Some minerals such as zeolites have an extremely open structure including channels through which ions of quite large dimensions can pass. The base exchange properties of zeolites depend on this and the same may apply to some clay minerals. Ions can thus enter the lattice without having to overcome any high energy barrier and the potential reactivity is increased.

Many of the properties of crystalline solids are greatly influenced by the presence of defects in the crystal lattice. Internal diffusion as well as surface reactivity is among the properties greatly affected in this way. In addition to actual dislocations of the lattice the common defects are due to either the presence of impurities or the misplacing of ions. Disorder of this latter nature can be classified into two types, Frenkel disorder due to the presence of ions in interstices of the lattice, and Schottky disorder characterized by vacant positions in the lattice. Generally the presence of such defects increases the rate of internal diffusion of ions. This is, however, not invariably so and perhaps the most striking examples of the contrary effect occur when the presence of impurities can stabilize an otherwise unstable compound, e.g. the prevention of the $\beta$ to $\gamma$ inversion in calcium orthosilicate.

The structural instability produced in minerals which are undergoing polymorphic inversion can increase the rate of reaction. Quartz is of course the commonest mineral to undergo such transitions, the $\alpha - \beta$ inversion at 573°C. being well within the range of the temperatures of metamorphism. Hedvall (1938) has shown experimentally that the rate of diffusion of Fe$_2$O$_3$
through quartz is notably accelerated at temperatures around 573°C. It is conceivable that under conditions of declining metamorphism the rocks might remain approximately at this temperature for a long time and that the effect might consequently be considerable.

Hedvall has also shown experimentally that newly and rapidly formed crystals, referred to as being in the "nascent" condition, are generally much more reactive than those which have been "aged". Presumably this is largely due to the great number of imperfections "frozen" into the lattice during rapid formation. He has compared two reactions:

\[
\begin{align*}
\text{MgO} + \text{FeO.Cr_2O_3} &= \text{MgO.Cr_2O_3} + \text{FeO} \\
\text{MgCO}_3 + \text{FeO.Cr_2O_3} &= \text{MgO.Cr_2O_3} + \text{FeO} + \text{CO}_2
\end{align*}
\]

The second reaction takes place at 100°C. lower than the first and this Hedvall ascribes to the "nascent" state of MgO formed when MgCO_3 decomposes to form MgO and CO_2.

That the crystalline state of the reactants is of great importance in controlling the rate of reaction can be illustrated by some syntheses of forsterite which were made from different materials but with other factors kept as uniform as possible.

**Table I.**

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Forsterite Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Clino-enstatite + MgO</td>
<td>60—80%</td>
</tr>
<tr>
<td>B &quot;Meta-talc&quot; + MgO</td>
<td>50—70%</td>
</tr>
<tr>
<td>C Hydrous silica + MgO</td>
<td>50—70%</td>
</tr>
<tr>
<td>D Talc + MgO</td>
<td>30—50%</td>
</tr>
<tr>
<td>E Quartz + MgO</td>
<td>ca. 10%</td>
</tr>
</tbody>
</table>

All mixtures were heated to 1300°C. for 2 hours. Forsterite estimated from X-ray photographs by Dr. G. F. Walker.

The clino-enstatite used in reaction A had been recently synthesized and would have been in a "nascent" state. Although the temperature 1300°C. is well below the melting point it must be remembered that clino-enstatite melts incongruently to forsterite and a silica-rich liquid and that Mg_2SiO_4 is the primary form of magnesium silicate developed in the solid state.

What is referred to as "meta-talc" is talc which has been dehydrated by heating. It is mainly glass and gives an imperfect clino-enstatite pattern with X-rays. We would expect it to be in highly reactive form.

The hydrous silica and the talc used in reactions C and D would be dehydrated during the heating and again we would expect them to be in a highly reactive state.

The magnesium oxide used in all these reactions was a prepared "reagent" and would be regarded as "aged". When heated with natural quartz the reaction would be expected to be slow. Comparison of the reaction rates of quartz (reaction E) and hydrated silica (reaction C) with magnesia is very striking.

The factors which we have been considering—original disorder in crystals of minerals, the effect of polymorphic transitions or of the nascent condition—may play large or small parts in metamorphic reactions. However, there is no doubt that the influence of temperature is of the greatest importance. A rise in temperature increases the internal vibrational disorder, i.e. increases the internal diffusion. When this diffusion proceeds with such energy that it can overcome
the energy barrier imposed by the surfaces of crystals the minerals can re-
crystallize, and if other compounds of suitable composition are adjacent can
react and form new compounds.

Buerger (1948) has described this very clearly. "It is known that the
activation energy of grain growth in metals is about twice the activation energy
required to make the metal atoms diffuse through their own solid structure.
The reason for this evidently is that more bonds must be broken to transport
an atom across a crystal boundary than to merely pass it along in the same
structure. There is an important geological significance in this relation for it
implies that whenever the temperature is sufficiently high to cause spontaneous
growth of the crystals it is already maintaining a very high level of diffusion. In
this condition, the smaller atoms, at least, may be expected to be rather freely
migrating through the remainder of the structure of the crystal. Thus whenever
the rock is in a condition to recrystallize, it is also something of a blotter for
available atoms, thanks to temperature. It is, therefore, evident that wholesale
diffusion must play an important role in the transfer of chemical material in
metamorphism."

An indication of the temperatures necessary to produce these conditions is
given by examining the Tammann temperatures for the common minerals.
The Tammann point is the temperature approximately at which there is a rapid
increase in the mobility of lattice ions which thus allows reactions between
solids to proceed at an appreciable rate (Rees, 1954). Its value is given by
0.5Tm, where Tm is the melting point in degrees absolute.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Melting Point °C.</th>
<th>Melting Point °K.</th>
<th>Tammann Point °K.</th>
<th>Tammann Temp. °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>1713</td>
<td>1986</td>
<td>993</td>
<td>720</td>
</tr>
<tr>
<td>Anorthite</td>
<td>1550</td>
<td>1823</td>
<td>912</td>
<td>639</td>
</tr>
<tr>
<td>Albite</td>
<td>1118</td>
<td>1391</td>
<td>696</td>
<td>423</td>
</tr>
<tr>
<td>Orthoclase</td>
<td>1170</td>
<td>1443</td>
<td>722</td>
<td>449</td>
</tr>
<tr>
<td>Diopside</td>
<td>1371</td>
<td>1644</td>
<td>822</td>
<td>549</td>
</tr>
<tr>
<td>Enstatite</td>
<td>1557</td>
<td>1830</td>
<td>915</td>
<td>642</td>
</tr>
</tbody>
</table>

The minerals and the temperatures quoted in Table II may look somewhat
unrealistic but they illustrate the extreme case of the silica minerals, the range
of the felspars and give some indication of the thermal properties of pyroxenes.
The table is not intended to convey more than that at temperatures between
about 400 and 700°C, the lattice ions of many rock-forming minerals will be
sufficiently mobile to promote reactions even in the absence of a liquid phase.

It must be remembered that the figures quoted in Table II refer to
determinations made at atmospheric pressure. It would be hard to find
agreement on the degree to which they would be affected by pressure, both load
and stress. Buerger and Washken (1947) have made some exploratory
observations on this factor. They have shown that recrystallization of minerals
can be caused by plastic deformation but that this only happens if a certain
critical temperature is exceeded. This temperature varies with the mineral
and the amount of deformation.

We have been considering the possibility of metamorphic reactions taking
place in the absence of an aqueous phase. The effects of high pressure and the
presence of water are generally to increase the speed of reaction and to lower the
minimum temperature required. A striking example of this is shown by E. F.
Osborn (1953), who synthesized forsterite from magnesium oxide and quartz in
the presence of water vapour at a temperature of 600°C. and a pressure of 1100 pounds per square inch. The reaction was complete in from 2 to 3 hours. This can be compared with the much slower reaction shown by E in Table I under dry conditions at atmospheric pressure and a much higher temperature. The raw materials were of much the same size in both experiments. The effect of stress, or something that could have the same effects as stress, was also investigated by Osborn. In a pressure vessel which gave a steam pressure of 7000 lbs. per sq. in. and at a temperature of 350° sillimanite remained unchanged after 3 weeks. By rotating the pressure vessel, so that it acted as a kind of ball mill, partial alteration to kaolinite occurred in 3 days. The grinding of the sillimanite thus exposing fresh surfaces to alteration and the reduction of grain-size could perhaps have some resemblances to the effects of shearing stress.

Conclusions.
The purpose of this paper has been an attempt to demonstrate that metamorphic reactions can take place in the absence of water at temperatures well within the limits of those generally believed to exist in the higher grades of metamorphism. The factors which have been considered do not conflict in any way with the generally accepted ideas that the presence of water plays an extremely important part in the great majority of metamorphic reactions. Yoder (1955) has recently discussed this subject. It is also hoped that this paper has given an indication that a study of the chemistry of solids as applied to minerals could help in the consideration of geological problems of many kinds.

References

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