3 July 1964, Volume 145, Number 3627 SCIENCE

Geological Aspects of High-Pressure Research

High-pressure experimentation is providing a new look at problems in geophysics and petrology.

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Mineralogical studies at high pressures and temperatures are greatly increasing our understanding of the earth's interior. A large number of minerals and other compounds which are stable only at high pressures can now be synthesized. Experimental study of minerals and mineral assemblages which have restricted stability ranges together with analytical study of rocks are providing a quantitative understanding of the conditions under which earth processes such as volcanism and metamorphism take place. The chemical composition of the earth's mantle and the variation of pressure and temperature with depth are approximately known, and within these broad boundaries to experimentation an understanding of the mineralogical constitution of the mantle is rapidly developing.

Modern high-pressure techniques make it possible to subject a substantial volume of material to static pressures as high as 100 to 150 kilobars (*1*) at controlled temperatures up to 2000°C. This pressure is not high in proportion to the pressure of 3600 kilobars at the center of the earth, but it makes possible experimentation at pressures and temperatures existing in the earth at depths up to 300 to 400 kilometers.

The zone between the earth's surface and a depth of 400 kilometers is in many ways the most interesting part of the earth. All but a small proportion of earthquakes take place in this depth range. Most of the radiogenic heat which is the fundamental energy source for such major geologic processes as metamorphism, volcanism, and mountain building also originates in this zone. Basaltic lava that has been erupted in great volume throughout geologic time in both continental and oceanic areas is believed to originate at a depth of about 100 kilometers. Moreover, there is a variety of discontinuities in the velocity of transmission of seismic waves in this depth interval (Fig. 1). Since the velocity of seismic waves is a function of rock type, such discontinuities indicate either changes in bulk chemical composition or pressure-induced phase transitions.

Mineral Transitions at High Pressure

Some of the pressure-sensitive transitions in minerals and mineral assemblages discovered in recent years are shown in Table 1. Constants for the pressure-temperature curves are given where possible; some reactions have not been studied in detail, and only approximate pressure ranges for them can be listed. Many other transitions are suspected on the basis of petrographic, crystallographic, or thermodynamic evidence.

The minerals listed under "low-pressure phase or phases" in Table 1 are chiefly silicates whose crystal structures consist of low-density, open networks of atoms. The commonest of these are quartz and the feldspars, which are the most abundant minerals in the earth's crust in continental areas. Less common minerals of this type are cordierite, nepheline, and leucite. The aluminosilicates in this group generally have the aluminum ion in fourfold coordination with oxygen. The stability fields of these minerals vary, but with the apparent exception of potassium feldspar none can exist at pressures greater than those present in the earth at a depth of 100 kilometers. In contrast, the products of high-pressure transitions tend to be minerals with more closely packed structures such as garnets, pyroxenes, kyanite, and forsterite. Some of these like jadeite, pyrope, and kyanite are stable only at high pressures. In these high-pressure phases, aluminum tends to be in sixfold coordination. These pyroxenes, olivines, and other dense minerals will probably undergo transitions to still denser phases, mostly in the pressure range above 100 kilobars. Two such transitions, the inversion of the iron olivine, fayalite, to a spinel structure and the inversion of coesite to stishovite (Table 1) have been realized experimentally.

Depth of Metamorphism

The stability fields of such high-pressure minerals as jadeite, kyanite, and aragonite indicate either that sediments and volcanics have been metamorphosed at much greater depth than has hitherto been supposed or that pressures in the crust resulting from orogenic forces were considerably greater than the hydrostatic load. Kyanite is commonly found as essentially pure Al_2SiO_5 in regional metamorphic rocks in many parts of the world. Inasmuch as the temperature of formation for such rocks is on the order of 300° to 600°C,

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the kyanite-sillimanite curve given in Table 1 shows that these rocks have crystallized at pressures over 9 kilobars. Under hydrostatic conditions this would correspond to a minimum depth of burial of 30 to 35 kilometers.

Kyanite is not unique in indicating high crystallization pressures for some metamorphosed sediments. Jadeite has been identified as a common constituent of the metagraywackes of the Franciscan series in California (*2*) and of similar rocks in Japan (*3*). Metagraywackes are known from other continental areas, and it is probable that further study of these rocks will reveal more occurrences of jadeite. Jadeite in veins in the Franciscan rocks is virtually pure $NaAlSi_2O_6$. The assemblage jadeite + quartz is also found in the groundmass of the graywackes. The reaction albite $\rightleftarrows$ jadeite + quartz takes place at even higher pressures than those required to stabilize jadeite in the absence of quartz (Table 1). The jadeite in the groundmass assemblage, however, is alloyed with about 25 percent of such components as $CaMgSi_2O_6$ and $NaFeSi_2O_6$, which should reduce the minimum pressure required to form jadeite + quartz. The high-pressure carbonate, aragonite, has also been found in these jadeite-bearing rocks. Aragonite can form metastably from aqueous solutions at atmospheric pressure, but it is unlikely that relatively coarse-grained aragonite with a metamorphic fabric has formed metastably in these Franciscan rocks.

Metagraywackes like those of the Franciscan series have probably crystallized at lower temperatures than kyanite schists and gneisses. Even if the temperature were as low as 200°C, the minimum pressure of formation indicated by the presence of pure jadeite is 5 kilobars; aragonite would require a pressure of 7 kilobars. Under hydrostatic conditions these pressures imply that the minimum depth of formation is 20 to 25 kilometers.

High-pressure data thus suggest that sedimentary rocks may be buried and metamorphosed at depths equivalent to the lower levels of the earth's crust in nonorogenic areas. However, seismic evidence indicates that the crust thickens from about 35 kilometers in stable shield areas to at least as much as 50 kilometers in mountain roots. It is in orogenic areas where thick series of strata have been folded into mountain ranges and roots that the process of metamorphism would be expected to take place.

Nevertheless, many geologists are reluctant to believe that metamorphic rocks have formed at depths where the hydrostatic pressure was more than 5 to 10 kilobars. If a rock now exposed at the surface was metamorphosed at a depth on the order of 20 to 30 kilometers, then obviously a very great thickness of sediments and volcanics must have been deposited on top of it and subsequently removed by erosion. Estimates of the thickness of a sedimentary sequence eroded from a particular area can sometimes be obtained by extrapolation from adjacent areas where there has been less erosion. In some cases these estimates fall far short of the depths indicated by the high-pressure data. However, such estimates have large uncertainties because sedimentary strata have extremely variable thickness in geosynclinal areas. Moreover, there is clearly a considerable thickening of the crust by folding and other deformation in orogenic areas.

The assumption that the pressure under which a rock crystallized is equivalent to that generated by overburden cannot be strictly correct, and it is possible that the departure from hydrostatic conditions is significant. Metamorphic rocks show abundant evidence of deformation by plastic flow. The pressure during metamorphism is,

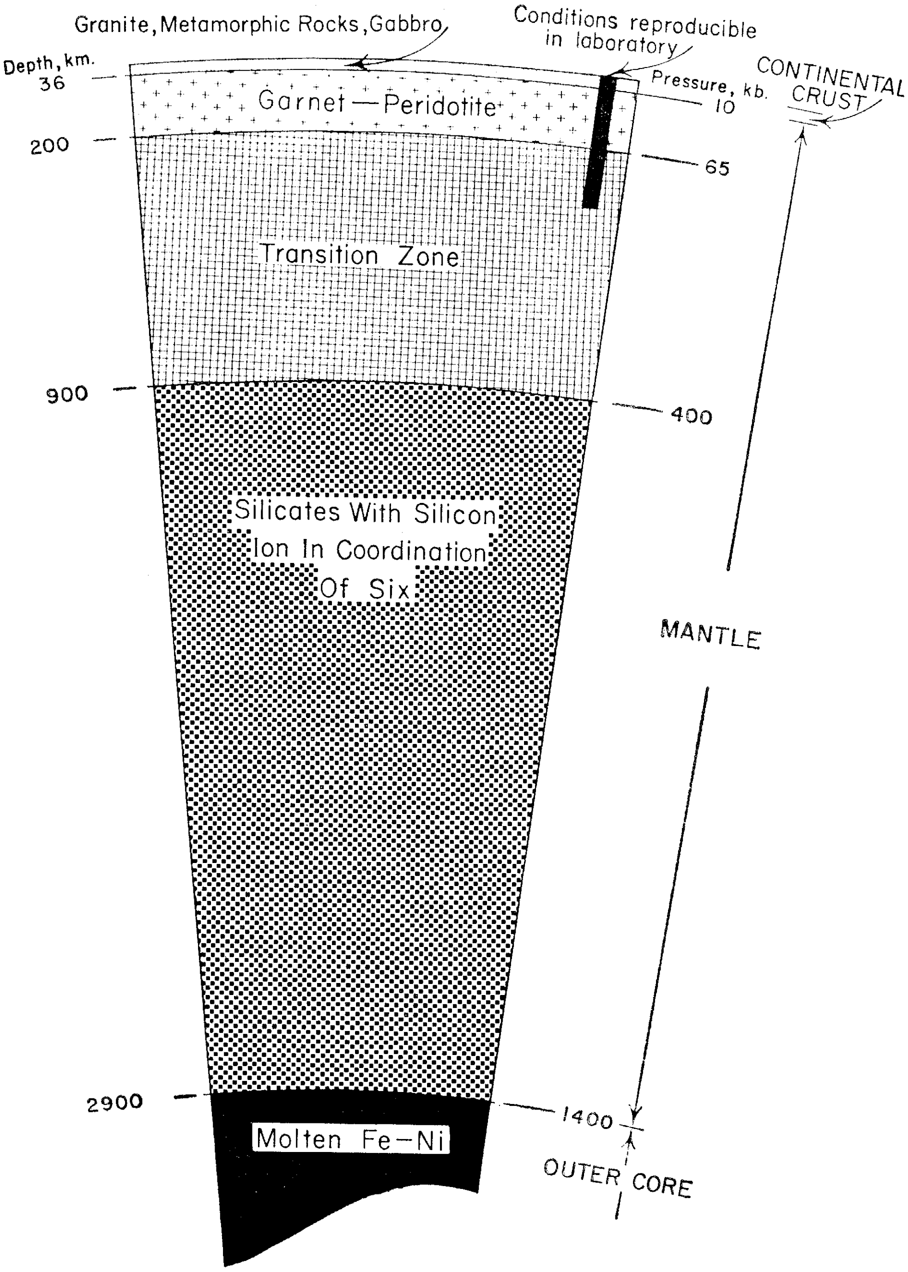

Fig. 1. Seismic discontinuities in the earth with probable rock types.

therefore, equal to the pressure generated by overburden plus an increment of pressure sustained by the strength of the rocks flowing under compression. Clark (*4*) has called this increment "tectonic overpressure." There has been much experimental study of the strengths of rocks at pressures and temperatures equivalent to those in the lower part of the crust. Hard rocks such as granite and basalt have strengths on the order of 10 kilobars at 500°C and confining pressure of 5 kilobars in short-term laboratory tests (*5*). The rate at which rocks are deformed in nature, however, is many orders of magnitude less than the strain rate in laboratory experiments. Heard (*6*) has shown that decreasing the strain rate greatly decreases strength in experiments at moderately high temperatures. The strength of the Yule marble at 500°C decreases from about 2 to 0.5 kilobars when the strain rate is decreased from 10^{-1} to 10^{-7} per second. Heard estimates that the strength of the Yule marble at this temperature would be on the order of 10^{-6} kilobar at a reasonable geologic strain rate of 10^{-14} per second. If harder rocks show a proportional decrease, tectonic overpressures could not be significant during metamorphism except, perhaps, under unusual conditions of high pressure and low temperature. Nevertheless, the matter is uncertain because of the large extrapolations involved.

Table 1. Phase transition in anhydrous minerals at high pressure.

Bulk composition	Low-pressure phase or phases	⇌	High-pressure phase or phases	P(kb) = a + bT(°C)		Ref.
				a	*b*	
C	Graphite		Diamond	14.4	0.027	(*30*)
$CaCO_3$	Calcite		Aragonite	5.5	0.0126	(*31*)
SiO_2	Quartz		Coesite	21.2*	0.0122	(*32*)
SiO_2	Coesite		Stishovite	97.5†	0.0203	(*33*)
Al_2SiO_5	Sillimanite		Kyanite	4.5*	0.0143	(*4*)
$Mg_3Al_2Si_3O_{12}$	Enstatite + sapphirine + sillimanite		Pyrope	4.9	0.0123	(*34*)
$NaAlSi_2O_6$	Albite + nepheline		Jadeite	1.0	0.0185	(*35*)
$NaAlSi_3O_8$	Albite		Jadeite + quartz	6.0	0.020	(*36*)
$CaAl_2Si_2O_8$	Anorthite		Grossularite + kyanite + quartz	30 kb at 1530°‡		(*37*)
$KAlSi_2O_6$	Leucite		K feldspar + kalsilite §	−9.7	0.0358	(*38*)
$NaAlSiO_4$	Nepheline		Nepheline II + jadeite	$P > 10$ kb		(*39*)
	Leucite + enstatite		Forsterite + K feldspar	$P < 10$ kb		(*14*)
$Mg_2Al_4Si_5O_{18}$	Cordierite		Enstatite + sillimanite + quartz	10–20 kb		(*40*)
Fe_2SiO_4	Fayalite		Spinel structure	30–60 kb		(*41*)

* The values for *a* and *b* are revised to eliminate a friction correction of −8 percent used in the original descriptions of these data. † Point at 130 ± 5 kb and 1600° ± 100°C established by experiment; slope calculated. ‡ Slope not determined. § K feldspar + kalsilite stable below 272°C at atmospheric pressure.

The Upper Mantle

The chemical and mineralogical constitution of the upper mantle and the nature of the Mohorovičić seismic discontinuity (*M* or Moho) which marks the transition of crustal rocks to mantle rocks have been the subject of spirited discussion in the past 10 years. Two views persist from this discussion. One view is that the upper mantle consists predominantly of peridotite or garnet peridotite. According to this theory the *M* discontinuity is then a compositional change from the granite, basalt, and metamorphic rocks of the crust to olivine-pyroxene rocks in the mantle. The alternative hypothesis is that the upper mantle has the same chemical composition as basalt but that under high pressure it forms a garnet-pyroxene rock called eclogite. The crust in oceanic areas is most likely basaltic below a thin skin of sediments, and it is possible that in continental areas the predominantly granitic and metamorphic rocks exposed at the surface grade down into rocks of basaltic composition at depth. According to this theory the *M* discontinuity is a phase transition from feldspar-bearing basaltic rocks in the lower crust to denser garnet-pyroxene eclogite in the mantle but with no change in bulk chemical composition at the discontinuity.

A variant of the peridotite hypothesis is that the mantle has a chemical composition similar to the silicate fraction of chondritic meteorites. Chondrites are feldspathic peridotites and pyroxenites with about 10 percent plagioclase feldspar; at the high pressures prevailing at depth in the upper mantle a rock of average chondrite composition would crystallize to a mixture of olivine, sodic pyroxene, and a trace (?) of garnet. The chondrite theory is attractive because chondrites contain a metallic phase, an Fe-Ni alloy, as well as a silicate fraction. There is thus an analogy with the Fe-Ni phase believed to comprise the earth's core and the silicate materials that make up the mantle.

Before coming to a consideration of the *M* discontinuity itself, it is worthwhile to summarize the geophysical, geochemical, and petrological facts that have a bearing on the problem of the constitution of the upper mantle (*7*).

The velocities of seismic waves in the upper mantle provide the most direct information about its constitution thus far obtained. Seismic velocities for a wide variety of rocks have been determined by experiment at high temperatures and pressures (*8*), and these may be compared with velocities observed for the mantle. Such studies show that the mantle is essentially crystalline since it will transmit shear waves and that the velocities for the upper mantle are consistent with experimentally determined velocities for rocks ranging from peridotite through eclogite. The seismic methods are not sensitive enough to differentiate between rocks in this range of composition.

The concentration of U, Th, and K in any model of the mantle has to be sufficient to account for the heat flow observed in oceanic areas but not so large that the heat generated by their decay will melt the mantle. It is uncertain whether convection plays a part in transferring heat in the mantle, and it is probable that these radioactive elements are concentrated in the upper part of the mantle. In a general way, however, the concentration of radioactive elements in terrestrial dunite and peridotite seems too low for a reasonable model, whereas their concentration in basalt seems too high. The abundance of radioactive elements in chondrites and in a single sample of eclogite from Hawaii seems about right (*9*). It is not clear why the eclogite should be less radioactive than basalts of similar bulk composition.

Three types of rocks now exposed at the surface are known to have come from the mantle. Basalt is one of these, but the mantle rocks from which the lava is derived either could have the same chemical composition as basalt or could be more mafic. Partial melting of some peridotites would be expected to produce a liquid of basaltic composition, just as would complete melting of an eclogite. Nevertheless, a peridotite of average chondrite composition does not appear to be a very likely parent material for basalt. The silicate assemblage in chondrites is decidedly odd. Feldspathic peridotites of terrestrial origin generally contain calcic plagioclase, whereas the feldspar in chondrites is notably sodic. Miyashiro (*10*) has shown that the plagioclases in a number of Japanese chondrites have compositions that group closely around 90 percent albite and 10 percent anorthite. A rock with a feldspar containing 90 percent albite could never yield a liquid with a normative feldspar containing 40 percent albite (characteristic of basalt) by partial fusion at low pressures. One cannot be so categorical about the fusion relations at high pressures where the soda would be present as the jadeite component in pyroxene rather than as feldspar. However, there is now no evidence to indicate that high pressure would reverse the relationship found at low pressures in which sodium is concentrated in the liquid relative to calcium.

Coarse-grained inclusions are occasionally erupted in suspension in basaltic lava, and some petrologists have argued that these are fragments of the mantle (*11*). It is, however, possible that the inclusions have crystallized from the basalt itself at depth and are therefore not directly derived from the mantle. The constancy of composition of these inclusions is frequently cited in the literature and it seems to have been overemphasized; in fact, the inclusions range from gabbro (in rare cases eclogite) to dunite but most commonly consist of olivine, pyroxene, and a chromian spinel.

A third type of rock that originates in the mantle is an intrusive ultramafic breccia called kimberlite. The presence of diamonds in kimberlites indicates that they have been erupted into the crust from a depth of at least 100 kilometers. The kimberlites have been severely altered within the crust, but their primary minerals—which are principally olivine, pyroxene, and pyrope-rich garnet—indicate that they were originally garnet peridotite. Kimberlites also contain a magnesian mica, phlogopite, which by conventional textural criteria appears to be primary. The concentration of phlogopite in kimberlites is sufficiently great to give these rocks a K_2O content about equal to basalt and substantially higher than most ultramafic rocks. This would probably make kimberlites too radioactive to be typical specimens of upper mantle rock.

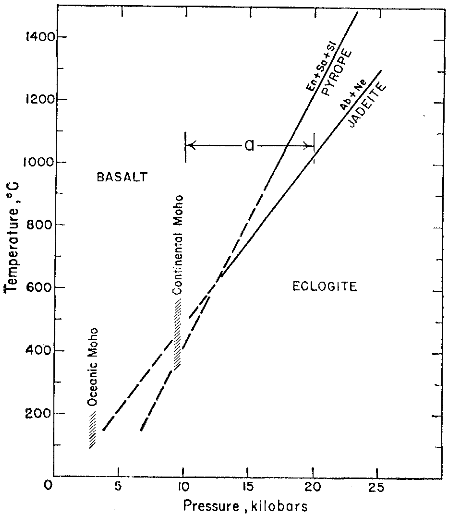

Fig. 2. Estimated position of the basalt ⇄ eclogite transition. The interval *a* is a bracket on the transition established by experiment with natural basalt (*14*). The width of *a* should not be confused with the actual width of the transition zone, which has not yet been established. Ab, albite; En, enstatite; Ne, nepheline; Sa, sapphirine; Si, sillimanite.

Many models for the mantle are based on the assumptions that the upper mantle is relatively homogeneous and that it is dry. Neither of these assumptions can be strictly true, and it may be that inhomogeneity and water content are significant factors.

It is uncertain whether or not the mantle was ever completely molten. If it has not melted, original inhomogeneities may still be present. Moreover, the process of volcanism tends to produce inhomogeneities. If basalt forms by partial fusion of a parent rock intermediate between basalt and peridotite, then the residue left after separation of the basalt will be more mafic than the parent rock. In the likely event that some of the basalt fails to reach the surface it will crystallize as eclogite at depth or as gabbro in more shallow intrusives. Hence, we might expect the upper part of the mantle to be a hodgepodge of rocks varying from gabbro and eclogite to peridotite and dunite. Indeed, the inclusions found in basalts represent just such a hodgepodge.

Green and Ringwood (*12*) have recently called attention to the possible importance of amphibole in the uppermost levels of the mantle in oceanic areas. Seismic velocities measured in amphibolite are slightly less than the values determined for peridotite or eclogite. But a peridotite could be partly hydrated to amphibolite without significantly reducing the velocity.

If the mantle has never completely melted (*13*), rocks at depth have dehydrated slowly through volcanic activity. In such circumstances, the minimum value to which the vapor pressure of water in the mantle could drop would be controlled by the permeability of the oceanic crust and uppermost levels of the mantle. There would be a tendency for water in the mantle to equilibrate with water at the bottom of the oceans, where the average pressure is about 350 bars.

Amphibolite is stable relative to basalt up to a temperature of 600°C at a water vapor pressure of only 1 bar. At a vapor pressure of 350 bars amphibolite is stable up to about 800°C (*14*). The effect of maintaining a constant vapor pressure on a system while increasing the lithostatic pressure is usually a reduction in the field of stability of a hydrous phase. This effect would thus combine with the increase in temperature with depth to eliminate hydrous phases below the uppermost part of the mantle. There is, however, good reason to suspect that there may be some hydrous phases such as amphiboles in mantle rocks to depths perhaps as great as 100 kilometers, particularly beneath the oceans.

The Basalt-Eclogite Transition and the *M* Discontinuity

The upper mantle is evidently composed of peridotite, eclogite, or an intermediate rock type, but available evidence does not permit more precise identification. Local inhomogeneities are probably present, and there is a good possibility that hydrous phases such as amphiboles may be important constituents in the upper 100 kilometers of the mantle. Nevertheless, the possibility exists that eclogite is the dominant rock type and that the Mohorovičić discontinuity is a phase change from basalt to eclogite. This theory has been attractive because it seems to offer a simple explanation for a wide range of geologic phenomena (*15*), but there are serious objections to it of a geophysical and petrological nature.

Eclogite is 10 to 15 percent denser than basalt, and for this reason it has long been regarded as a high-pressure form or "facies" of basalt. A sample of basalt can be converted to a garnet-pyroxene assemblage typical of eclogites by heating it for an hour at 1200°C at a pressure in the range of 20 to 30 kilobars.

Although synthesis of eclogite is easy, the stability field of eclogite relative to basalt has not yet been adequately determined. The pressure-temperature boundary between eclogite and basalt is a complex transition zone rather than a univariant curve because of the large number of chemical components in the system. This transition zone lies between 10 and 20 kilobars at temperatures in the range 1000° to 1200°C (*14*), but the width of the zone and its slope are not yet established. The reaction rate of the transition is sluggish below 1000°C, and attempts to flux it with water usually cause melting of the sample or hydration to amphibolite.

In the absence of more complete data on this transition the stability curves of pyrope and jadeite can be used as an approximation (Fig. 2). The pyrope in eclogitic garnets is alloyed with iron and calcium end members that are stable at atmospheric pressure. Similarly the jadeitic pyroxenes in eclogites contain a large fraction of diopside that is also stable at atmospheric pressure. The effect of these alloying components should be to cause the basalt-eclogite transition to lie at lower pressure than the boundary curves for pure pyrope and jadeite (Fig. 2). The pyrope and jadeite curves are close together and near the high-pressure limit for the basalt-eclogite transition established by experiments with natural basalt and eclogite. Most likely the basalt-eclogite transition zone has a slope similar to that of the pyrope and jadeite curves, and is located in a pressure range a few kilobars below these curves.

The thermal gradient in the earth, and the temperature range at the *M* discontinuity are most uncertain. Calculation of the gradient requires a knowledge of the concentration and distribution of radioactive elements at depth in the crust and mantle, and this distribution is not well known. The temperature uncertainties for the base of the continental and oceanic crusts (Fig. 2) may well be too small. The uncertainty in the location of the basalt-eclogite transition zone, particularly at temperatures below 700°C, is also quite large. There is, however, an approximate fit between the expected pressure-temperature range of the transition zone and the expected pressure-temperature range of the *M* discontinuity. Even if the uncertainties were negligible, these data would not prove that the *M* discontinuity was due to a basalt-eclogite phase transition. They do prove that the upper mantle is predominantly in the eclogite facies, and they suggest that the phase-change hypothesis is a possible interpretation. Nevertheless, there are geophysical and petrological observations which do not support the hypothesis.

The most serious objection is that the observed depth of the *M* discontinuity in continental and oceanic areas cannot be correlated with variations in the flow of heat from the earth's interior. The average heat flow at the earth's surface is approximately the same in oceanic and continental areas, namely, 1.2×10^{-6} calorie per square centimeter per second. However, there are large regional variations particularly in oceanic areas. The heat flow measurements in the Pacific Ocean basin vary from 0.14 to 8.09×10^{-6} cal cm^{-2} sec^{-1} (*16*). Heat flow that is higher than average indicates a steep thermal gradient, and if the discontinuity were a phase transition, areas of high heat flow should be underlain by a thicker than usual crust. Both Bullard and Griggs (*17*) and Wetherill (*18*) have computed the variation in crustal thickness expected from variation in heat flow in various models in which the *M* discontinuity is assumed to be a phase change. Wetherill's calculations show that an increase in heat flow of only 50 percent through an oceanic crust bounded by a phase transition should increase its thickness from 7.5 to 30 kilometers. Yet seismic studies of the crust in the Pacific show that its thickness is relatively constant in the range 5 to 10 kilometers (*19*). The only way around this argument is to assume that areas of high heat flow cover shallow heat sources of volcanic origin. Since the variations of heat flow in the Pacific are on a regional scale, and since they can be correlated with major topographical features of the ocean floor, this assumption would not be very plausible.

Bullard and Griggs (*17*) have also shown that the approximate agreement between the basalt-eclogite transition and the expected pressure-temperature conditions at the *M* discontinuity under the oceans and continents (Fig. 2) is only apparent. Temperature-depth curves for continental and oceanic crusts are imprecisely known, but if it is assumed only that the heat flows in continental and oceanic areas are approximately equal and if at least 5 percent of the heat flow in continental areas is generated in the crust, then the temperature-depth curves for the continents and ocean basins must intersect at less than the depth of the *M* discontinuity under the continents. Under these conditions it is impossible to draw a smooth phase-transition curve that will intersect the calculated temperature-gradient curves for oceanic and continental areas at the required depths, with eclogite being stable at greater depth than basalt at both points of intersection.

Occurrences of eclogite included in sialic metamorphic rocks are known from many continental areas. If it could be established that some of these eclogites were metamorphosed in place, then obviously at such times the basalt-eclogite transition lay within the crust and not at its base. Unfortunately, the geological relations are not usually clear enough to eliminate the possibility that the eclogites were intruded in the solid state from some greater depth. Nevertheless, a similar argument can be made with reference to the kyanite-sillimanite transition.

Comparison of the curve for the kyanite-sillimanite transition given in Table 1 with the estimated position of the basalt-eclogite transition in Fig. 2 shows that if the pressure in a metamorphic sequence is high enough to stabilize kyanite it must also be high enough to convert basalt to eclogite. Rocks of basaltic composition are quite commonly interstratified with kyanite schists and gneisses, but they have usually crystallized as amphibolite rather than as anhydrous gabbro or eclogite. In such cases the vapor pressure of water was high enough to mask the eclogite transition. Kyanite rocks are very common in regional metamorphic areas throughout the world. Only under special circumstances could they have been underlain by gabbro with a transformation to eclogite at the *M* discontinuity. The geothermal gradient would have to have curved so that it intersected the kyanite-sillimanite transition three times. The geothermal gradient probably has a slope not far different from the slope of this transition, and therefore this is not an impossible situation. But it does seem improbable that it would be the general case in regional metamorphic areas.

Thus to reconcile the phase-transition hypothesis with these geophysical and petrological observations requires a number of questionable assumptions.

The Lower Mantle

Although seismic velocities observed for the upper mantle can be matched with velocities determined by experiment for various ferromagnesian silicates, the velocities in the lower mantle are too high to be explained by any natural rock-forming silicates. The transition from peridotite-eclogite rock in the upper mantle to the higher-velocity materials at greater depth was formerly called the "20 degree discontinuity." However, it is now believed that the discontinuity is not sharp but is a progressive change in the nature of mantle rocks beginning at a depth of about 200 kilometers and extending to 900 kilometers (*20*).

In 1936 Bernal (*21*) suggested that this discontinuity might be due to the inversion of olivine to a spinel structure. The inversion should result in a density increase of approximately 10 percent. Because seismic velocities increase with density in an isochemical series, the inversion should produce a substantial increase in velocity.

Since the time of Bernal's original suggestion much experimental data and thermodynamic argument have shown that the olivine-spinel transition is a reality. No one has yet synthesized a spinel form of the magnesian olivine, Mg_2SiO_4, but spinel forms of other olivines such as Fe_2SiO_4, Ni_2SiO_4, Co_2SiO_4, Mg_2GeO_4, and Ni_2GeO_4 (*22, 23*) have been prepared as well as solid solutions of some of these compounds with Mg_2SiO_4. Spinel solid solutions containing up to 70 percent Mg_2SiO_4 have been synthesized (*23*). The pressure range in which pure Mg_2SiO_4 olivine will invert to a spinel form can be estimated from thermodynamic data obtained from these phase studies. Various estimates suggest that this inversion will be found in the range 100 to 150 kilobars. This is now the upper limit of static pressure techniques, a probable reason why Mg_2SiO_4 spinel has not thus far been synthesized.

Stishov and Popova (*24*) have reported the synthesis at 120 kilobars of a form of SiO_2 with rutile structure in which silicon has a coordination number of 6. This phase has formed under natural conditions in sandstone shattered by meteorite impact and it has been named stishovite (*25*). The increase in the coordination number of silicon to 6 produces a very large increase in density. The density of stishovite is 4.34 compared to 2.65 for quartz or 2.92 for coesite.

The discovery of stishovite has increased speculation that at sufficiently high pressure silicates may break down to oxides plus stishovite. The assemblage MgO (periclase) + SiO_2 (stishovite), for example, would be about 10 percent denser than Mg_2SiO_4 spinel. A number of other reactions are possible.

Ringwood and Seabrook (*26*) have shown that germanate analogues of silicates will invert to high-pressure forms at pressures less than those necessary to produce inversions in the corresponding silicates. They have synthesized a variety of germanate pyroxenes with ilmenite structure in which the germanium ion has sixfold coordination. Their results indicate that the sequence of transformations to be expected with increasing pressure in a silicate pyroxene such as enstatite might be:

$$\text{MgSiO}_3\ (\text{pyroxene}) \rightleftarrows \text{Mg}_2\text{SiO}_4\ (\text{olivine}) + \text{SiO}_2\ (\text{stishovite})$$

$$\text{Mg}_2\text{SiO}_4\ (\text{olivine}) \rightleftarrows \text{Mg}_2\text{SiO}_4\ (\text{spinel})$$

$$\text{Mg}_2\text{SiO}_4\ (\text{spinel}) + \text{SiO}_2\ (\text{stishovite}) \rightleftarrows \text{MgSiO}_3\ (\text{ilmenite})$$

The density increase associated with transformations to ilmenite structure in germanate pyroxenes is in the range 15 to 20 percent. The expected transformation pressures for silicate pyroxenes cannot now be accurately predicted, but it is reasonable to suppose that the transformations will occur in the pressure range of 100 to 400 kilobars, which is the range of the transition zone in the mantle. If $MgSiO_3$ with ilmenite structure proves to be a reality, there is a possibility that at sufficiently high pressure pyrope-garnet ($Mg_3Al_2Si_3O_{12}$) would invert to a solid solution between $MgSiO_3$ (ilmenite) and Al_2O_3 (corundum).

Thus it appears probable that the transition zone in the mantle between 200 and 900 kilometers is produced by a series of reactions in which the olivine, pyroxene, and garnet of the upper mantle are replaced by silicates in which silicon is in sixfold coordination. There is probably a succession of reactions rather than a single transition, and each individual reaction will take place over a depth interval because of solid solution in the phases involved. These reactions form an interesting parallel to the sequence of metamorphic reactions found in crustal rocks in which minerals with aluminum in fourfold coordination, like feldspar and cordierite, are progressively replaced by high-pressure phases such as jadeite, pyrope, and kyanite, in which the aluminum is in sixfold coordination. Thermodynamic reasoning and studies with model structures such as germanates provide a broad picture of the transition zone. But it is hoped that static and dynamic high-pressure techniques will progress to the point where silicates can be directly studied at the required pressures and temperatures. Only in this way can we obtain a detailed understanding of the transition zone.

Effects of Pressure on the Melting of Silicates

Increase of pressure greatly increases melting temperatures in silicate systems and it also produces pronounced changes in the character of melting. Silicates which melt congruently at one pressure may melt incongruently at another pressure. Changes in solid solubility, the appearance of high-pressure phases, or the disappearance of low-pressure phases are all reflected in the liquidus and solidus surfaces in multi-component systems. Determination of such phenomena provides knowledge of the melting behavior of rocks at depth in the mantle and puts useful limits on estimates of the present temperature gradient in the earth's interior.

Melting curves for the pure minerals diopside, enstatite, pyrope, and albite in the range up to 50 kilobars (Fig. 3) have a pronounced curvature and their slopes above 25 kilobars are only about half the initial slopes. The Simon equation,

$$P = A\,[(T/T_0)^c - 1],$$

where A and c are adjustable constants and T_0 is the melting point at atmospheric pressure, can be fitted to these data and constants for the curves are given in Table 2. The congruent melting curve of pyrope (Fig. 3) has

Table 2. Constants for the Simon equation for silicate melting curves.

Mineral	T_0 (°K)	A (kb)	c
Enstatite	1830	28.5	5.01
Diopside	1665	23.3	4.64
Albrite	1391	19.5	5.1

been determined only in the range 36 to 50 kilobars, and this is not a sufficient range to show any curvature; the slope in this range, however, is similar to the slopes of the diopside and enstatite curves. Pyrope is not stable on the liquidus of the system MgO–Al$_2$O$_3$–SiO$_2$ below 36 kilobars; spinel is the liquidus phase for pyrope composition from atmospheric pressure to 36 kilobars. The liquidus curve for pyrope composition is nearly linear, and the initial slope is notably less than that of diopside, enstatite, or albite. Comparison of these curves with the fusion curve of iron given in Fig. 3 illustrates the fact that silicates generally have steeper melting curves than have metals.

These silicate melting curves indicate that, although the melting temperatures of rocks should markedly increase with depth in the mantle, the rate of increase will be much less at greater depths. This effect can be illustrated by supposing, for the moment, that the solidus curve for the mantle is similar to the diopside and enstatite curves. The initial slopes of these curves are on the order of 15°C per kilobar. If these slopes were linear to a pressure of 1400 kilobars at the core-mantle boundary, a temperature on the order of 20,000°C would be required to melt silicates at that depth. However, if the Simon equation is used to extrapolate the curves to 1400 kilobars, both give a melting temperature of about 3750°C. The Simon equation predicts that the curvature will persist to higher pressures.

Unfortunately the problem of estimating melting temperatures at depth in the earth is a much more complicated matter than simple extrapolation of these melting curves. Use of the Simon equation, which has little theoretical basis, is a major uncertainty. Within the range of present measurements, the Simon equation can be fitted to the melting curves of most pure silicates, metals, and alkali halides. But there are a number of exceptions. Melting curves with negative slopes or maxima cannot be described by the Simon equation. Substances that have polymorphs with negatively sloped melting curves such as bismuth are well known. Maxima have been found on the fusion curves of cesium, rubidium, and graphite (*27, 28*). Moreover, use of the Simon equation to predict the melting behavior of rock in the mantle means using an equation developed to describe the melting curve of a pure phase as an equation for the solidus curve for a multicomponent system. More theoretical and experimental work is evidently needed to establish a sound basis for extrapolating melting curves to higher pressures. Nevertheless, until such information has been obtained, the Simon equation remains the best available means of extrapolation.

Clark (*29*), and Newton, Jayaraman and Kennedy (*27*) have called attention to the fact that the dT/dP slope of a eutectic or minimum melting curve in a multicomponent system should be less than the slopes of the melting curves of the pure end members of the system. This effect is due to the fact that although there is a significant entropy of mixing in the liquid phase, even in an ideal solution, the volume of mixing of most liquids is negligible. The effect will be reduced if there is solid solution among the solid phases, because the entropy of mixing of the solids will tend to cancel the entropy of mixing in the liquid phase.

There are insufficient data to predict the effect of entropy of mixing on a solidus curve in any system of geologic interest, and the possible significance of the effect must be evaluated by experiment. That the effect can be significant is shown, for example, by data on the system Na–K where the slope of the eutectic is notably flatter than the slopes of the melting curves of pure Na and K (*27*). Whether or not the effect is significant in silicate systems in general or in mantle rocks in particular is not now very clear. Initial slopes for the liquidus in silicate systems as low as 6°C per kilobar have been determined (for example, pyrope, Fig. 3), but in the cases studied thus far these low slopes cannot be unambiguously related to an entropy-of-mixing effect.

The most direct solution to the problem would be to determine experimentally the solidus curves for probable mantle rocks; that is, garnet peridotite and eclogite. Yoder and Tilley's (*14*) preliminary data for the slope of the eclogite solidus in the range 20 to 30 kilobars indicate a slope of 12°C per kilobar. Attempts to determine the solidus for a peridotite at high pressure have not thus far been successful because of quenching difficulties.

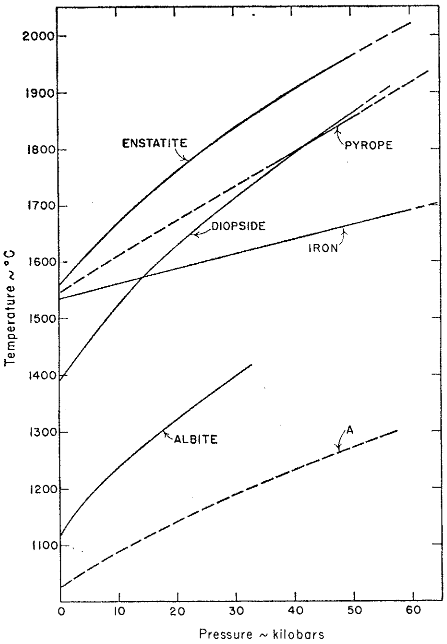

Fig. 3. Effect of pressure on the melting of some silicates and Fe. Curve *A* is a solidus curve for the upper mantle estimated by Clark (*29*). A small incongruent melting field and the pressure-temperature curve for the transition protoenstatite ⇄ rhombic enstatite, both at low pressures, have been omitted from the enstatite curve. References: diopside and albite (*42*), Fe (*43*), pyrope (*34*), enstatite (*44*).

A further problem in estimating the solidus curve for the mantle is introduced by the presence of the transition zone in the upper mantle. As already indicated, this transition zone is mostly likely produced by the reaction of olivine and pyroxene in the upper mantle to denser silicates, probably forms in which the coordination of the silicon ion shifts from 4 to 6. When a melting curve is intersected by a transition of this sort it is inflected to higher temperatures. The transition zone in the mantle is probably a series of reactions so that the solidus should be inflected upward in steps. In the lower mantle below the transition zone, the dT/dP slope of the solidus should gradually lessen.

Clark (*29*) has recently calculated the effect of the transition zone on an estimated melting curve for the mantle. Using the Clapeyron and Simon equations with numerical quantities taken from experimental and geophysical data, he obtained a curve that indicates a melting temperature of 7500°C at the base of the mantle. Extrapolations that fail to take account of the influence of the transition zone indicate a temperature about half as high, and it is evident that the effect of the transition zone is quite large. Clark estimated that uncertainties in the numerical quantities he used lead to an uncertainty in the melting temperature at the base of the mantle that is within 2000°C. However, he pointed out that his model does not take account of a possible shift in the coordination of the silicon ion in the liquid phase as well as in the solid phases. Should such a shift occur in the liquid phase at pressures present in the lower mantle, the slope of the melting curve would be lessened and the estimated melting temperature at the base of the mantle would be too high.

Summary

The low-density minerals that make up the bulk of rocks in the earth's crust, such as quartz and the feldspars, are transformed by high pressure into much denser phases. In some cases the products of these transitions are new phases that were first discovered in the laboratory; in other cases they are minerals such as kyanite, jadeite, and pyrope, which have long been known as constituents of metamorphic rocks. Determinations of the stability fields of these high-pressure minerals show that either metamorphism of sedimentary rocks takes place at much greater depth than has hitherto been supposed or pressures generated by orogenic forces may have significantly augmented the hydrostatic pressure. The second alternative seems unlikely, but lack of information on the strength of rocks during metamorphism makes the matter uncertain.

Geophysical and petrological observations indicate that the dominant rock type in the upper mantle is garnet peridotite. However, there is reason to believe that the mantle is inhomogeneous and that a variety of rocks ranging in bulk composition from eclogite to peridotite are present. Hydrous phases, such as amphiboles, are possible constituents in the upper 100 kilometers. The hypothesis that the Mohorovičić discontinuity is a dynamic equilibrium between basalt and eclogite seems improbable.

The transition zone between the upper and lower mantle can be explained as a series of reactions in which silicates with the silicon ion in fourfold coordination are transformed into phases in which silicon is in sixfold coordination. This interpretation is supported by synthesis of stishovite, a polymorph of SiO_2 with rutile structure, and by syntheses of germanate pyroxenes with ilmenite structure.

Data on the melting of silicates at pressures up to 50 kilobars show that the initial dT/dP slopes of silicate melting curves are much steeper than those of metals but that they show considerable curvature. The increase of melting temperature with pressure should be much more pronounced near the top of the mantle than at greater depth.

References and Notes

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