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RECENT GEOCHEMICAL RESEARCH AT HIGH PRESSURES

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INTRODUCTION

Investigations of the stability relations of silicates at high temperatures and atmospheric pressure were begun about 1900. These studies have been fundamental to our understanding of the origin and evolution of volcanic rocks and other rocks of igneous origin which solidified near the surface. Deep-seated igneous rocks and many metamorphic rocks cannot be completely understood on the basis of such experimentation, however. Geochemical research at high pressure is needed to advance our knowledge of the processes which produce most of the material making up the earth.

Studies of mineral stability at high pressures indicate that some rocks, now exposed at the earth's surface, acquired their present mineralogy at high pressures. The data give a measure of the amplitude of the vertical movements which have affected the crust of the earth in geologic time. The unexpected result is that these movements have been a few tens of kilometers, i.e., of the order of the thickness of the crust itself.

High-pressure geochemical research has also been important as a supplement to seismology. The velocities of elastic waves in the earth provide a most important body of information about its constitution. Considerable ambiguity remains, however, and this can be removed to some extent by chemical considerations. Geochemical studies will aid in interpreting the Mohorovicic discontinuity at the base of the crust and the rapid increase with depth of the seismic velocities between 400 and 1000 km. In addition, measurement of the effect of pressure on melting points, in conjunction with seismic evidence of the essential solidity of the outer part of the earth, set a limit to the temperatures between depths of 30 and 100 km.

The following section of this review is concerned with observational seismology and its interpretation in terms of laboratory measurements of the velocities of elastic waves in rocks. This is followed by a discussion of the methods and apparatus of highpressure geochemistry, and then by discussions of various parts of the earth's interior together with relevant experimental data. This paper is largely concerned with experiments made at pressures about 10 kilobars; Roy and Tuttle⁽¹⁾ have reviewed earlier work at lower pressures.

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This review is premature in the sense that many important investigations are unfinished and many problems have yet to be investigated. But this is characteristically the case in a field which has recently been opened and which is advancing rapidly. The methods used, the principles involved, and the information sought are well illustrated by work which is now in more or less final form.

SEISMIC DATA

Two types of bodily elastic waves can be propagated in an isotropic elastic medium. Their velocities as functions of depth form one of the most important bodies of information about the interior of the earth. If Vp denotes the velocity of compressional waves and Vs that of shear waves, the theory of infinitesimal elasticity yields the relation 18

$$V_{\rm P}^2 - \frac{4}{3} V_{\rm S}^2 = K_{\rm S}/\rho$$
 ,

where K_S is the adiabatic bulk modulus and ρ is the density. The quantity K_S/ρ , sometimes called the elastic ratio, is very nearly equal to $K_T/\rho \equiv (\partial P/\partial \rho)_T$. Here P is pressure and K_T the isothermal bulk modulus. $(\partial P/\partial \rho)_T$ can be derived from conventional measurements of static compressibility; a correction amounting to a few per cent is needed to convert the results to adiabatic conditions, but it is easily made to sufficient accuracy. Comparison of laboratory and seismic results then leads to notions about the constitution of the earth's interior.

This method of analyzing seismic data suffers from the disadvantage that the observed velocities must be subjected to mathematical manipulations, often with compounding of observational errors. At shallow depths, V_P is much better known than V_S , but the greater accuracy of V_P is lost in forming the quantity K_S/ρ . These objections have been overcome by direct measurements of V_P at pressures up to 10 kilobars by an ultrasonic pulse technique. Such measurements were first made by Hughes and his collaborators. (2-4) More extensive results, both with regard to number of types of rock investigated and with regard to attention to anisotropy of the specimens, has recently been published by Birch. (5) Some 200 individual specimens are included in the latter study. The velocities are determined by measuring the transit times of ultrasonic pulses in cylindrical specimens of rock. The data are accurate to a few parts in a thousand; this accuracy is ample since different cylinders cut from the same chunk of rock may differ by more than 1 per cent.

Seismically determined velocities of compressional waves in the earth's crust range from somewhat more than 5 km/sec near the surface to 7 km/sec or so at depth. A large number of common types of rock have velocities in this range, and no difficulty is encountered in reconciling these data with plausible compositional models of the crust. On the other hand, no unique model can be found from seismic data alone. There is also ambiguity in the seismic results themselves. The increase in velocity with depth in the crust may be uniform or it may take the form of stepwise jumps at the interfaces between uniform layers.

It is clear, however, that in "normal" continental regions of moderate elevation a more or less abrupt increase in velocity takes place at a depth of 30 to 35 km. This is the Mohorovicic discontinuity, which by definition marks the base of the crust. Beneath the oceans it is found at depths (below sea level) of 10 to 15 km, and its depth may exceed 60 km beneath high mountain ranges. An outstanding problem is its sharpness; present seismic data cannot distinguish between a true discontinuity in the mathematical sense and a transition spread over an interval a few kilometers thick. Read for the second state

Beneath the Mohorovicic discontinuity, velocities of compressional waves range from 8 km/sec upwards. Few minerals are known to have such velocities at the relevant pressures. In particular, the framework silicates of low density, such as quartz and feldspars, fail to satisfy the seismic requirements although they are common at the surface. Dense phases, relatively low in silica, such as olivine, pyroxene, and garnet, have the required elastic properties.

At depths between about 400 and 1000 km the seismic velocities increase with depth at an unusually rapid rate. An analysis by $Birch^{(6)}$ indicates that the velocity gradient is too large to be attributed to compression of a homogeneous material. This region of the earth must then be characterized by a change in composition, phase, or both. Using an equation of state derived from finite-strain theory, Birch extrapolated the elastic properties of the material below 1000 km to low pressure and found that the seismic velocities were higher than those found in dense silicates. The elasticity of oxides such as MgO or Al_2O_3 is consistent with the extrapolated data. The most plausible interpretation of this result is that the lower portion of the earth's mantle is composed of dense polymorphs of silicates, which are unknown at the earth's surface.

HIGH-PRESSURE GEOCHEMISTRY

There is no rigorous relation between pressure and depth in the earth. The usual approximation is to regard the earth as composed of a heavy liquid and to calculate the pressure as if it were hydrostatic. This approximation may fail badly near the surface, but at depths greater than, say, 20 km it becomes fairly accurate because the mean pressure becomes large compared with the strength of the rocks. This "lithostatic" approximation leads to a calculated pressure of about 9 kilobars at the depth of the Mohorovicic discontinuity in continental regions. At a depth of 400 km the pressure is about 140 kilobars, and at 1000 km it is roughly 400 kilobars. This, then, is the range of pressures in which several interesting geophysical phenomena take place. The upper end of the pressure range is unfortunately not yet attainable in apparatus which generates static pressure.

Most materials of geochemical interest are silicates, and reactions among them take place sluggishly. Temperatures of 1000°C or more are often required if reactions are to occur in hours rather than weeks. This means that high pressures and temperatures must simultaneously be maintained for long periods of time. High pressures generated by shock waves do not last long enough for reaction to take place. In most cases the phases present at high pressure and temperature can be quenched in and identified after the pressure has been released.

The first apparatus used in high-pressure geochemistry was an adaption of the 12 kilobar equipment used by Bridgman in much of his work. Modifications include the transmission of pressure by an inert gas rather than an oil, and enlargement of the bore of the pressure vessel to accommodate an internal furnace. Apparatus of this type has been described by Yoder. (7) The pressure range was later extended by a similar modification of Bridgman's 30-kilobar apparatus. (8-10)

Equipment of this sort is capable of high precision in the measurement of both pressure and temperature. Pressure can be determined to within a few bars by the change in resistance of a coil of manganin wire, and temperature can be closely measured with thermocouples. But this type of apparatus is inconvenient to use, and simpler, if less accurate, equipment has been developed. The earliest of these was a modification of Bridgman's anvil apparatus for use at high temperatures. ⁽¹¹⁾ This equipment is exceedingly simple to build and operate; it suffers from the disadvantages that the pressure on the sample may not be uniform and that it is heated by an external furnace. The latter feature limits its temperature of operation to about 900°C.

A number of these disadvantages have been overcome in the "single stage" apparatus developed by Boyd and England. ⁽¹²⁾ Their design has evolved from earlier equipment developed by Coes [described by Roy and Tuttle⁽¹⁾] and by Hall⁽¹³⁾. Talc is used to transmit the pressure, which must be calculated from the load on the piston. A correction is required for friction against the wall of the pressure vessel and for the finite strength of the talc; the first effect can be reduced by lubricating the walls with lead foil. The correction is determined by calibration against the bismuth I-bismuth II and thallium II-thallium III transitions. The first takes place at about 25 kilobars according to Bridgman, and the second at about 37 kilobars according to Boyd and England. ⁽¹²⁾ Both pressures correspond to room temperature.

An attractive feature of this apparatus is that it can serve as the basis for equipment designed to operate in the range up to 100 kilobars. But the problem of simultaneous measurement of high temperatures and pressures in such equipment is not completely solved. Temperatures are measured with thermocouples, but the junction is subjected mechanical distortions as well as high pressure. These may affect its calibration by an unknown amount. The mechanical strength of the pressure medium undoubtedly decreases at high temperatures, which means the correction to the pressure determined by calibration at room temperature is too large. Comparison with results obtained in other apparatus suggests that errors in pressure and temperature due to these effects are small above 20 kilobars and 1000°C, but there is evidence the pressure calibration depends on both temperature and pressure. (14) Pressures and temperatures have been found to be highly reproducible from run to run. (14, 15)

None of the equipment discussed above can achieve pressures above 50 kilobars at high temperatures. The modified anvil apparatus can go higher than this at temperatures below 600°C, but only the "single stage" can reach pressures above 30 kilobars at temperatures above 1000°C. Efforts to extend the pressure range are being made in several laboratories devoted to geochemical research, but routine work above 50 kilobars has not yet been achieved. Research in this direction will surely continue because of interest in the properties of the earch at depths greater than 400 km.

AMPLITUDE OF VERTICAL MOVEMENTS IN GEOLOGICAL TIME

The first experimental indication that rocks now exposed at the surface have been subjected to great pressures in the past came from determination of the stability relations of the pyroxene jadeite, NaAlSi₂O₆. ⁽¹⁶⁾ Nearly pure jadeite has been found in California, Japan, and Burma; if the mineral formed within its field of stability at temperatures above 100°C, pressures of at least 5 to 10 kilobars must have prevailed. A similar conclusion resulted from a study of the much more widespread mineral kyanite, Al₂SiO₅. ^(10, 14) Pressures of about 10 kilobars are necessary to form it stably at 300° to 500°C. It can be inferred from these results that pressures of the order of that at the base of the crust were involved in the production of jadeite and kyanite.

Experimental data for garnets and for certain pyroxenes near enstatite, MgSiO₃, in composition have yielded similar results. (¹⁷) Many garnets consist principally of solid solutions between almandine, Fe₃Al₂Si₃O₁₂, and pyrope, Mg₃Al₂Si₃O₁₂. Almandine is stable at relatively low pressures, but garnets containing over 50 per cent pyrope probably required pressures above 10 kilobars for their formation. Such garnets prove to be fairly common in nature. Enstatite can contain no more than 1 to 2 per cent Al_2O_3 in solid solution at atmospheric pressure. At 20 kilobars or so it can dissolve nearly 20 per cent Al_2O_3 and its composition may approach that of pyrope. Natural enstatitic pyroxenes have been found with up to 9 per cent Al_2O_3 , which again implies high pressures of formation.

These results imply either that metamorphic rocks now at the surface have been buried to depths of 30 km or so during metamorphism, or that during metamorphism pressures are systematically higher than those that would be found at equivalent depths in a heavy liquid. No choice between these alternatives can presently be made; much interpretation of these experimental results must still be done.

CONSTITUTION OF THE CRUST

Seismic velocities in the crust range from these characteristic of granitic to those characteristic of gabbroic rocks. Their dependence on depth is uncertain, but laboratory observations may be brought to bear on this question. If the mineralogical makeup of the crust or any part of it is uniform, the velocity will be virtually independent of depth below about 6 km. ⁽¹⁸⁾ The reduction in velocity due to rising temperature may be expected nearly to offset the increase due to rising pressure. Compositional layering could lead to stepwise increases in velocity, and a progress ive change in composition could survive the large vertical movements that seem to be recorded in rocks, unless they are the natural consequence of the increasing pressure and temperature at depth.

Two processes leading to an increase in velocity with depth suggest thems elves. The first follows from the observation that seismic velocities in pyroxenes are higher than those in amphiboles, or in micaceous minerals. $^{(5)}$ Micas and amphiboles contain water, but pyroxenes are anhydrous. If the hydrous minerals are broken down at depth, a stepwise increase in velocity could result. Another way of obtaining an increase in velocity with depth involves the decomposition of feldspar. Plagioclase feldspars are solid solutions between albite, NaAlSi₃O₆, and anorthite, CaAl₂Si₂O₆. In the presence of the pyroxene diopside, CaMgSi₂O₆, the albite component of the plagioclase may break down to jadeite and quartz. The jadeite will enter into solid solution with the diopside, and the increase in velocity resulting from the higher percentage of pyroxene in the rock will offset the reduction in velocity resulting from the hormation of additional quartz. But plagioclases high in anorthite have higher velocities than those rich in albite, so that this reaction should raise the velocity in the rock.

The above suggestions about the crust are but two of a number of possibilities. Neither has yet been investigated experimentally because of the chemical complexities involved. A special complication affects the dehydration reactions, since the vapor pressure of water need not be the same as the pressure experienced by the solid phases.

THE OUTER MANTLE

The outstanding problem here is closely connected with the cause of the Mohorovicic discontinuity. Does this feature result from a change in composition, phase, or both? Geologic evidence bearing on this question comes from the composition of inclusions brought up in volcanoes and diamond pipes. Inclusions of olivine, approximately Mg_2SiO_4 with some magnesium replaced by ferrous iron, and of eclogite, a rock consisting essentially of a jadeitic pyroxene and a magnesian garnet, are widespread. Evidence that the diamond pipes came from the mantle is provided by the presence of the diamonds themselves. If they formed in their field of stability, the rocks must have

come from depths greater than 100 km. Some of the volcanic eruptions in Hawaii are immediately preceded by earthquakes with focal depths of 20 miles or more. This is deeper than the Mohorovicic discontinuity beneath Hawaii. The pattern of the earthquakes strongly suggests that the lava is also originating in the mantle; it is known to contain inclusions of both olivine and eclogite.

The assumption that the outer mantle consists mainly of olivine, pyroxenes, and garnets is consistent with seismic data. In fact, these are the only abundant groups of minerals which have the requisite elastic properties. The Mohorovicic discontinuity is then to be regarded as due in part to a phase change, with a pyroxenefeldspar assemblage giving way to a different pyroxene and garnet. This is consistent with presently available data on the breakdown of albite and the appearance of garnets. But the reaction which is presumed to take place in the earth involves several phases, each of which is a solid solution. The problem in its full complexity has not yet been investigated in the laboratory. Another question concerns the behavior of anorthite. By itself it appears to be stable to very high pressures, but it may be consumed by reaction with another phase, for example enstatite, in the earth.

THE MANTLE BELOW 400 KILOMETERS

One of the earliest interpretations of the rise in velocity between 400 and 1000 km was made by Bernal, $^{(19)}$ who noted that two polymorphs of Mg₂GeO₄ exist. One is isostructural with olivine and the other, which is about 10 per cent denser, has the spinel structure. Bernal suggested that an analogous transition in olivine, which would be s pread over an interval of depth by solid solution, might account for the behavior of the seismic velocities in this part of the earth.

This question has been investigated by Ringwood^(20, 21) and by Dachille and Roy. ⁽²²⁾ They have mainly studied this inversion in solid solutions of Mg_2SiO_4 in Mg_2GeO_4 or Ni₂GeO₄. The conditions under which pure Mg_2SiO_4 might be expected to invert were estimated by extrapolation. In addition, Ringwood⁽²¹⁾ produced the olivinespinel inversion in the mineral fayalite, Fe₂SiO₄. The results of these investigations roughly confirm Bernal's hypothesis, but the accuracy of the experimental data is not high. There is great incentive to develop equipment in which the possible olivinespinel inversion in Mg₂SiO₄ can be studied directly.

MELTING RELATIONS UNDER PRESSURE

The fact that a measurable amount of energy is carried by transverse elastic waves in the outer mantle implies that the material here is mostly solid. On the other hand, the widespread occurence of basaltic lava, both at the present time and in the past, shows that liquids may readily be generated locally. This suggests that melting is closely approached in the outer mantle, which in turn implies that inferences about temperatures in the earth can be drawn from melting relations of rocks at high pressures.

The mean slopes of the melting curves of the pyroxene diopside, the feldspar albite, and the garnet pyrope are, respectively, 10° to 13°, 11°, and 14°C/ kilobar. (17, 23, 24) The similarity in the slopes is striking in view of the differences in crystal structure and other physical properties of these minerals. Theoretical considerations suggest, however, that the effect of pressure on minimum melting points in multicomponent systems is smaller than in these cases, in which melting occurs as in a one-component system. Little work on more complicated systems has been done at high pressure. Preliminary data by Boyd and England⁽¹⁷⁾ on the system $MgO-Al_2O_3-SiO_2$ indicate that the effect of pressure on the minimum melting point is less than 6°C/kilobar, a figure that is considerably smaller than those for the pure phases.

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DISCUSSION

by F. Dachille

It is of interest to observe that although the existence of an olivine-spinel polymorphic pair of Mg₂GeO₄ was reported by V.M. Goldschmidt⁽¹⁾ in 1931 the spinel form could not be verified and hence was doubted more or less completely by a number of workers until clearly demonstrated by Roy and Roy. (2) With this beginning, and interested in the geophysical importance of a transition of the olivine-spinel type by the suggestion of Bernal and the more elaborated one of Mason, (3) work was started in 1955 in this laboratory to study this transition by well established methods of phase equilibria in the system Mg₂GeO₄. The necessary pressure variable in the study of the solid solution fields soon went beyond the 80,000 psi working limits of the cold seal hydrothermal apparatus(4) but consistent results were obtained in the pressure-temperature region of the uniaxial apparatus. Thus it was possible to present to the 1956 Geological Society of America Meeting the p-t-x relations of the system summarizing the first high pressure work done on an olivine-spinel transition and illustrating the geologically important finding that the substitution of Fe²⁺ for Mg²⁺ broadened the spinel phase field in any isobaric section. Work continued for two more years and was reported in 1958, and later published. (5-6) Some of the findings will be of interest here. An isothermal section in this system at 550°C, the temperature selected in order to avoid the interference of hydrous phases and to stay within reasonable limits of the strength of the tool steel pistons (of the Speed Star or HS66 type), gave the positions of the spinel and olivine solid solution field boundaries (and the separating 2 phase field) to about 60 kb. At the highest experimental pressure the spinel composition contained

MELTING AND OTHER PHASE TRANSFORMATIONS AT HIGH PRESSURE

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INTRODUCTION

The fusion curves of the four Group VIII metals nickel, iron, platinum and rhodium and the phase diagrams of bismuth and rubidium have been determined to 100, 000 atm.* The volume changes which occur at the melting points for the Group VIII metals were calculated from the initial slopes of their fusion curves. This volume increment has been directly measured for iron only and the present data agree with the directly measured value. The phase diagram for bismuth was of interest because of its complexity and because it proved to have a conveniently located transformation at room temperature which now serves as a pressure reference point at about 120,000 atm. Rubidium was expected to have an electrical resistance cusp at about 130,000 kg/cm² similar to the one for cesium at 55,000. Such a cusp was not found but its fusion curve was unusual in that it showed a maximum.

THE FUSION CURVES OF NICKEL, IRON, PLATINUM AND RHODIUM

The different types of samples used in melting point determinations are illustrated in Figs. 1, 2, 5 and 6. In the designs of Figs. 1 and 2, the detection of melting was by a sharp increase in electrical resistance, the occurrence of a maximum millivolt reading on a Ni-Ni 20 per cent Co junction (in the case of nickel) or a latent heat step in a rising temperature-time curve. The resistance change associated with melting for iron is quite small so in order to detect it unmistakably probe wires drawn from the same pure iron that was used for the specimen were inserted near the center where the sample was hottest and melting first occurred. The voltage drop across these wires due to the heating current in the rod showed a sharp increase at the melting point. Examples for these means of detection are illustrated in Figs. 3 and 4.

*Unless otherwise stated, pressures quoted in this article are based on the electrical resistance transitions observed by Bridgman on Bi, Tl, Cs and Ba.

53 mole per cent Mg_2SiO_4 . Extrapolation to the closure of the 2 phase field, that is, at 100 mole per cent Mg_2SiO_4 , results in a transition pressure of 100 kb[±] 15 kb. This would be roughly equivalent to a depth 300 km below the surface of the earth.

Now the experimental p-t univariant slope of the olivine-spinel transition of the Mg₂GeO₄ end member⁽⁵⁻⁶⁾ is equal to 25° C/kb but a value of about 13° C/kb may be inferred (from the total p-t-x of the system) for the Mg₂SiO₄ end member. It will be seen that, if slopes of this range of values are plotted passing through a point at 550°C and 100 kb (⁺15 kb) and then compared to the various postulated temperature gradients with dept in the mantle, phase transitions of the olivine-spinel type certainly should be part of any consideration of the "400 km" discontinuity. These results strongly support Clark's remark on the need for equipment for the direct study of the inversion. Such studies on the pure forsterite and on a simplified assemblage of minerals to approximate the best deduced compositions of the mantle will be important contributions. What form this equipment will take is not too clear. In view of our experience, some of it represented in the discussion of G.C. Kennedy's "calibration" paper, the accuracy of the uncomplicated uniaxial type apparatus is certainly better with respect to temperature and appears to be as good as the best of the piston-cylinder pressurized gas types below 700°C.

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