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EXPERIMENTAL DETERMINATION OF JADEITE STABILITY RELATIONS TO 25,000 BARS*

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* Paper No. 147 published under the auspices of the Committee on Experimental Geology and Geophysics and the Division of Geological Sciences at Harvard University.

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* Paper No. 147 published under the auspices of the Committee on Experimental Geology and Geophysics and the Division of Geological Sciences at Harvard University. ABSTRACT. The reaction, albite + nepheline = 2 jadeite, has been studied experimentally at pressures between 10,000 and 25,000 kg/cm², and at temperatures between 600° and 1200°C. The pressure system is an enlarged version of Bridgman's double press, in which a conical high-pressure chamber is given external support by heavy rings. The pressure medium is nitrogen. Temperatures are produced by an internal wire-wound furnace, in which are heated small gold or platinum capsules containing the charges. Quenching is obtained when the furnace power is cut off. Charges of natural jadeite, natural albite plus synthetic nepheline, natural analcite, and synthetic jadeite glass have been heated for periods up to several hours under pressure, quenched, and examined with the aid of an X-ray diffractometer and under the microscope.

The equilibrium line for the reaction is considered to be satisfactorily represented by the equation, P = 1000 + 18.5 T, where P is the pressure in kg/cm², T the temperature in degrees centigrade. The uncertainty of the intercept for T = 0 is ± 1000 kg/cm², the uncertainty of the slope, ± 1 (kg/cm²)/degree. The experimental line is in reasonable agreement with the thermochemical data. Jadeite crystallizes on the highpressure side of this line from glass of jadeite composition, or from an albite-nepheline mixture. The position of the jadeite melting curve has been roughly determined.

The discussion relates these results to the question of the high-pressure breakdown of the feldspars, and to the possibility of accounting for the Mohorovicic discontinuity as a boundary for such transformations.

INTRODUCTION

The conditions of formation of the mineral jadeite have attracted much attention in recent years. Petrologically, jadeite is interesting not so much for the relatively rare occurrence of the pure mineral as for its presence as a component in the pyroxene, omphacite, which is found in eclogites. Eclogites have been thought to have formed at the highest pressures attained during regional metamorphism (Eskola, 1939), and until recently, despite many attempts, jadeite had not been synthesized. The highest pressure employed in the unsuccessful experiments, which have been reviewed by Yoder (1950b), appears to have been no greater than 4000 bars. Within the last few years jadeite has been produced experimentally at pressures greater than 10,000 bars in at least three laboratories, and it has become possible to begin a systematic exploration of its field of stability.

Jadeite (NaAlSi₂O₆) has a composition intermediate between that of albite (NaAlSi₃O₈) and of nepheline (NaAlSiO₄.) But whereas the latter minerals have framework structures and densities of about 2.6, jadeite has a pyroxene structure and a density of about 3.3; its compressibility is comparable with that of olivine (Adams and Gibson, 1929; Yoder and Weir, 1951.) The "jadeite problem" may thus be considered as part of a problem of much wider significance: the feldspar problem. The feldspars are with little doubt the principal minerals of the Earth's crust, that is, of the outermost shell which is bounded internally by the Mohorovičić discontinuity of the seismologists. Below this discontinuity the seismic velocities assume values which are definitely incompatible with the velocities in rocks containing

major proportions of any of the feldspars. There are two conceivable explanations: (1) a discontinuous change of composition, from gabbroic to ultramafic, with a drastic impoverishment of the subcrustal material with respect to alkalies and alumina; or (2) a change of crystalline phase, from feldspar to jadeitic pyroxene and other high-density minerals, especially garnets, with little immediate change of composition. Though the first possibility has won wide acceptance, the second, which is essentially a form of the "eclogite hypothesis," still deserves careful attention. This hypothesis originated with Fermor (1912, 1913, 1914, 1938) and has been advocated by Joly (1930, p. 53-54) and by Holmes (1945, p. 507.) The following study of the jadeite equilibrium is, of course, merely a first step in the experimental investigation of the eclogite equilibrium; further work must include at least lime and magnesia as additional components.

The thermochemical data relating to the jadeite equilibrium have been studied in several recent papers. The heats of formation of the required components have been determined by Kracek, Neuvonen, and Burley (1951), and the entropies by Kelley, Todd, Orr, King, and Bonnickson (1953.) These writers, as well as Yoder and Weir (1951), and Adams (1953), conclude that jadeite is stable with respect to albite plus nepheline at ordinary pressure and temperature; the equilibrium curve for the reaction ab + ne = 2jd has been computed by Adams and by Kelley et al.

The present work was begun in late 1952, and jadeite was first identified with certainty among the synthetic products in May, 1953. Unknown to us, a program of high-pressure synthesis had been in progress for several years at the Norton Company of Worcester, Masssachusetts, and jadeite, as well as pyrope, kyanite, and a new dense polymorph of silica (Coes, 1953, 1955), had been produced at pressures between 20,000 and 45,000 bars; the synthesis of jadeite was first accomplished in September, 1948.¹ The breakdown of analcite to jadeite, and to albite plus nepheline, at high pressures has been reported by Griggs, Kennedy, and Fyfe (1955a, 1955b). Kyanite and pyrope have also been crystallized in the course of the present work (Robertson, Birch, and MacDonald, 1955); their equilibrium relations will be discussed in other publications.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge our indebtedness for many kinds of assistance: to Dr. J. F. Schairer, of the Geophysical Laboratory, for supplies of synthetic jadeite glass and of synthetic nepheline; to Professors Clifford Frondel and C. S. Hurlburt, Jr., of Harvard University, for natural jadeite, albite, and analcite; to Dr. W. S. MacKenzie and Dr. J. V. Smith, of the Geophysical Laboratory, for carefully indexed diffractometer patterns of high and low albite; to Mr. F. R. Boyd, Jr., of the Geophysical Laboratory, for preliminary information concerning the breakdown of nepheline; to Dr. Sydney P. Clark, Jr., of Harvard University for carrying out several runs; to Professor J. B. Thompon, Jr., of Harvard University, for many helpful suggestions. The construction and frequent replacement of the high-pressure and

¹ Personal communication from Dr. Loring Coes, Jr.

high-temperature components were skillfully carried out by Mr. Harold J. Ames, Mr. Arthur Ames, and Mr. Donald Murphy.

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EXPERIMENTAL DETAILS

Pressure system.—The pressure system is closely patterned after a smaller one designed by Bridgman (1938) for use with liquids; the linear dimensions of our equipment are approximately 50 percent greater than those of Bridgman's apparatus. Thus the bore of the high-pressure chamber is 3/4 inch instead of 1/2 inch; this enlargement provides barely adequate space for an



Fig. 1. Arrangement and principal components of pressure system: A, tie rods and plates of press; B, lower ram; C, upper ram; D, supporting rings; E, high-pressure chamber.

internal furnace. The requirement of temperatures of the order of 1000°C excludes the use of liquids, and the pressure medium was either argon or nitrogen.

The principal components of the high-pressure system are (fig. 1) a framework (A) of plates and tie rods, a lower hydraulic ram (B), an upper hydraulic ram (C), the tapered high-pressure cylinder (E) and its support rings (D) (see also fig. 2.) Two pumps capable of producing liquid pressures of about 20,000 lbs/in² supply the two hydraulic systems. The upper ram forces a tungsten carbide piston into the bore of cylinder E to produce the internal pressure; at the same time, the lower ram forces E into the support rings D, to produce an external pressure over the tapered surface. The ratio of internal pressure to external pressure was usually maintained at about 3/1. Before pressure can be built up with this system, a preliminary compression of the gas raises the pressure from that of an ordinary commercial cylinder to about 20,000 lbs/in².

A number of details concerning packings, clearances, materials, and so on, were varied from time to time in efforts to eliminate leaks, and to improve the life of the parts and convenience of access. These have little general interest and will not be described here but they will be recorded in a separate report to the Office of Naval Research. It is perhaps worth recording, however, the most common type of mechanical failure. This was a rupture of the highpressure cylinder on a surface approximately normal to its axis and several inches from its small end, often accompanied by a radial fracture down the length. This type of rupture, which sometimes occurred at pressures as low as 12,000 bars, appears to be related to the discontinuity of internal pressure at the piston packing; below this packing, the pressure has its high value; above the packing, it is zero. At the same time, the external surface of the tapered cylinder is acted upon by the supporting pressure, which is not uniform but reaches its highest value near the small end. Improvement resulted from reducing the external pressure in the uppermost support ring by giving this ring a small amount of initial clearance, but it cannot be said that the difficulty has been finally eliminated.

The furnace (F in fig. 2) is assembled in a thin-walled steel tube which slips into the bore of the high-pressure chamber. The bore of the porcelain furnace tube is 1/4 inch, the length of winding about 3 inches on a diameter of 5/16 inch. The space between the winding and the steel tube is filled by a sleeve of "Lava" (mostly pyrophyllite, marketed by the American Lava Corp., Chattanooga) which serves as electrical and thermal insulation. Within the furnace bore is a multibore porcelain tube carrying thermocouples. The upper part of the furnace is closed by a solid plug, and all interior empty spaces filled with powdered alumina, in order to reduce convection. The furnace winding is connected at one end to the steel sleeve, which is grounded; at the other, along with the thermocouples, to insulated, pressure-tight stems in the bottom closure. In a convenient variation, a miniature socket connector is used as part of the furnace tube and makes an easily disconnected junction with the leads of the bottom closure. Also at the base of the furnace tube,



Fig. 2. Internal arrangements of high-pressure system: A, high-pressure cylinder; C, supporting rings; B, lower closure, with electrical leads; D, piston mushroom, with packing; E, piston; F, furnace.

below the heated region, is the manganin pressure gauge, and in some arrangements, a copper resistance thermometer.

The furnace winding is of nichrome, kanthal, or platinum-rhodium wire or strip, usually designed to have a hot resistance of about 13 ohms. The power input is controlled by a variable transformer supplied by a constant voltage transformer with a capacity of 1 KVA.

Measurement of pressure and temperature.—Though rough measurements of pressure may always be made from the ratio of areas of piston and ram and the pressure on the ram, the uncertainties resulting from friction and distortions may be large; the pressures given in this work depend upon the change of electrical resistance of a manganin coil exposed to gas pressure.

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The high-pressure scale depends upon fixed points established by Bridgman (1940), of which we have used the freezing pressure of mercury, 7640 kg/cm² at 0°C and 12,000 kg/cm² at 22°C, and the transition pressure for the bismuth modification I to II, 25,800 kg/cm² at 22°C.² These pressures are probably accurate to about one part per thousand. With the aid of these fixed points, Bridgman has shown that the resistance of manganin wire is not quite linear with pressure: if the coefficient of a manganin coil is determined at the freezing point of mercury and then used, by linear extrapolation, to measure the bismuth transition pressure, the error is about 2 percent. This would not be a significant error for the present work; it can, moreover, be eliminated by the use of a second-degree relation between resistance and pressure. The principal uncertainty of pressure measurement in this work arises from the effect of temperature upon the resistance of the manganin gauge coil.

Between 20° and 30°C, the resistance of manganin passes through a flat maximum with respect to temperature, and in ordinary installations of manganin pressure gauges it is rarely necessary to correct for small changes of ambient temperature. In the present system, however, the gauge may reach temperatures as high as 100°C, which depend upon the power input and the duration of heating. As the coil temperature rises at constant pressure, its resistance decreases, giving the appearance of a drop in pressure. It became necessary to determine the temperature of the coil, and also to examine the effect of temperature upon the resistance-pressure characteristic of manganin.

The pressure gauges were 50-ohm coils of no. 40, double-nylon-covered manganin wire recently obtained from the Driver-Harris Company, wound non-inductively on Teflon spools, and protected by Teflon sleeves. The sensitivity of resistance measurement corresponded to a pressure difference of 10 kg/cm². A number of these coils were calibrated against the freezing point of mercury at 0°C at various times; the pressure coefficient is $2.31 \cdot 10^{-6}$ per kg/cm² at room temperature, with variation of about 0.5 percent. (Coils made of enameled manganin wire obtained from the same manufacturer about twenty years ago show a coefficient of about $2.5 \cdot 10^{-6}$ kg/cm².) Several coils were then heated to temperatures up to about 125° C at 1 atmosphere, and also at 7500 kg/cm², measurements of resistance being taken as function of both temperature and pressure. The results are summarized in table 1. The effect of temperature is slightly smaller at 7500 kg/cm² than at 1 atmosphere, with the corollary that the pressure coefficient is slightly larger at 100°C than

t°C	and Pressure Coeffici R/R ₂₅	ent of Resistance of Manganin Increase of pressure coefficient, percent
25	1.0000	0
50	0.9998	_
75	0.9991	0.81
100	0.9979	1.67
125	0.9965	2.7_{7}

TABLE 1 Effect of Temperature on the Electrical Resistance

² The unit of pressure for the experimental work is the kg/cm², which equals 0.98 bar; the difference between these two units is of no consequence for the present work.

at 25°C. The effect of changing the temperature, at constant pressure, from 25°C to 100°C is equivalent to a pressure change of approximately 900 kg/cm². An error in the temperature of the coil of 5°C at 100°C is equivalent to a pressure change of roughly 100 kg/cm². The cumulative errors may amount to as much as several hundred kg/cm² at the highest pressures.

For comparison with table 1, Bridgman (1938, p. 170) gives an increase of coefficient of 0.6 percent between 30° C and 75° C; an earlier and probably less satisfactory determination (Bridgman, 1935, p. 79) gives an increase of 1.3 percent between 0 and 50° C, 2.0 percent between 0 and 95° C. There is some evidence that the temperature coefficient of the pressure coefficient is more variable than the pressure coefficient itself.

The temperature of the pressure gauge in our high-pressure system was obtained from the change of resistance of a copper coil mounted close to the pressure coil and having the same external dimensions; it was supposed, for this correction, that the slope of the resistance-temperature curve of copper is unaffected by pressure, in accordance with Bridgman's determination (1931, p. 262; 1938, p. 174) of the small effect of temperature upon pressure coefficient. A rough value of the coil temperature may also be obtained from the temperature of the base of the tapered cylinder.

Temperatures in the furnace were determined by thermocouples, usually with at least two junctions close to the charges. The temperature is far from uniform; it varies from as much as 1200° C or so at the hottest region to about 100° C at the cylinder wall, less than 1 cm distant radially, and to about the same temperature at the ends of the furnace, 3 or 4 cm distant axially. The best location for the charges was determined by trial. Most of the uncertainty in the temperature of the charges arises from the sharp variation of temperature along the furnace; unless the charges were accurately centered upon the locus of maximum temperature, the variation along a single charge might reach 50° or more. By placing the charges between two thermocouple junctions, we attempted to bracket the actual temperature, but the uncertainty remains appreciable.

Chrome-alumel couples were first used, with leads of chromel and alumel through the packing of the bottom closure to an external cold junction. The effect of pressure on the thermal electromotive force of this couple has been shown to be negligible up to 4000 kg/cm² and 600°C (Birch, 1939); the pressure has been extended to 7000 kg/cm² in unpublished work. It has been assumed that the pressure effect is still relatively unimportant at the higher pressures of the present study. Under ordinary conditions, the chromel-alumel couple may be used to some 1100-1200°C, but there is evidence of some kind of deterioration in high-pressure nitrogen at temperatures of 900°C and higher. This became noticeable as an apparent decrease of temperature at constant power input and constant pressure, and it has been tentatively ascribed to nitriding of the alumel wire. The effect disappeared when platinum-platinum-10% rhodium couples were substituted for chromel-alumel. A pressure effect has been noted for this couple, amounting to an apparent decrease of about 12°C for 20,000 kg/cm² and 1000°C on linear extrapolation from the measurements at lower temperatures and pressures (Birch, 1939).

A further uncertainty was introduced by the use, with this couple, of copper leads through the bottom closure. This made the connection from couple to copper inside the pressure chamber the effective cold junction, for which the temperature was taken as equal to that of the copper coil described above. This particular correction has been eliminated in later work by the use of platinum and platinum-rhodium leads through the packing. The major uncertainty as to temperature arises from non-uniformity of the temperature distribution, as mentioned above.

Materials.—The determination of the jadeite equilibrium line depends chiefly upon the crystallization of synthetic glass of the composition of jadeite, prepared by Dr. J. F. Schairer of the Geophysical Laboratory of Washington. Several other materials used for various purposes were as follows:

- Nepheline, synthetic, also prepared by Dr. Schairer. An analysis of this material is given in Kracek and others (1951.)
- Albite, Amelia, Virginia. An analysis of another sample from this locality is given in Kracek and others (1951).
- Quartz, Lisbon, Maryland. This is described in Kracek and others (1951).
- Analcite, Cape Blomidon, Nova Scotia, A sample of very pure analcite from the Holden Collection, Harvard University.
- Gibbsite, synthetic, Norton Company, Worcester, Mass. This is a commercial product; it was heated for 3 hours at 110°C in order to remove excess water, before use.

Jadeite, Burma, no. 10464 of the Holden Collection, Harvard University.

Procedure.—Finely ground samples weighing about 50 milligrams were loaded into 5/8-inch lengths of gold or platinum tubing, 1/8-inch in diameter; these capsules were either left unsealed, with crimped ends, or sealed by arcwelding according to procedures developed by Yoder at the Geophysical Laboratory. Three or more of these capsules could be packed in the furnace, between thermocouple junctions.

As in most studies of silicate equilibrium relations, advantage has been taken of the sluggishness of the reactions: after an exposure to the highest temperature of an hour or so (see table 2), the charges were quenched to ordinary temperatures while still under pressure by the simple method of cutting off the power to the furnace. The transfer of heat in the dense nitrogen is so rapid that the temperature falls to about 100° C (or the temperature of the steel cylinder) in a matter of seconds, and it is assumed that no significant change of phase takes place in this time. The pressure was then reduced, and the charges removed for examination.

In the beginning of an experiment, the pressure was raised with the furnace cold, to a pressure somewhat below the desired final pressure. The temperature was then raised to the desired point over a period of about 1 hour; with the increase of temperature of the nitrogen, the pressures also increased, usually by 1000 to 2000 kg/cm². The pressure and temperature were then kept as constant as possible at the maximum values, which are the ones indicated in table 2. It is assumed that, whatever reactions occur during the heating period, the final products correspond to the conditions of maximum

temperature. This assumption appears to be justified by the results. When the products are assigned positions in the pressure-temperature diagram according to the highest pressures and temperatures, there is a clear separation of fields, which could hardly result if the rate of heating or duration of heating had a significant effect. It may be noted furthermore that the approach to the high temperature is in all cases made by way of the jadeite field, as determined below, and similarly, on quenching the charge is returned to the jadeite field. Charges crystallized in the abite-nepheline field, however, showed no jadeite in the product.

Identification usually depended upon comparison of X-ray diffraction patterns taken with a Norelco high-angle recording diffractometer. In some cases this was supplemented by microscopic determination of refractive index with the aid of immersion oils. Because of the purity of the starting materials, the number of possible products was small, and it was usually possible to account for all significant lines in the diffractometer pattern. The amount of crystallization, when the initial ingredient was glass, varied from zero to about 50 percent, with individual grains up to about 0.1 mm but usually smaller than 0.05 mm. The whole charge was generally used for the X-ray sample; it was then scraped from the mount and saved for possible future examination.





Fig. 3. Diffractometer patterns of Burmese jadeite and of synthetic jadeite and corundum formed from jadeite glass and gibbsite at about 800°C and 20,000 bars. The ordinate is 2θ (CuK α). The corundum lines are labeled CO.

parison between the patterns of natural Burmese jadeite and of synthetic jadeite crystallized from synthetic jadeite glass plus a small amount of gibbsite.

RESULTS

The fields of stability can be roughly outlined with the aid of observations of the behavior of natural minerals. On heating in the (ab + ne) field, natural jadeite breaks down to these minerals; similarly, on heating in the jadeite field, a mixture of albite and nepheline begins to form jadeite. The reactions are slow, especially below about 900°C, and never reach completion in the present experiments, even with the aid of such catalysts as water, gibbsite, or sodium fluoride. The results are significant only if a change of phase can be definitely established; this requires some minimum amount of transformation, possibly 5 to 10 percent. In about one-half of the runs starting with the crystalline phases, in which a change might be expected, the transformation could be observed. Only these significant results are plotted in figure 4; they suffice to fix a low-pressure limit for the reaction, given by P = 19 T (P in kg/cm², T in degrees Centigrade.) They are consistent with a line drawn through 0°C and zero pressure, having a slope of 20 bars/deg or 50 deg/kilobar, as given by the thermodynamic data. On the other hand, because of the wide separation of the significant points at the lower tempera-



Fig. 4. Transformations of natural minerals in the temperature-pressure plane of jadeite composition. The starting materials were either Burmese jadeite or Amelia albite plus synthetic nepheline, as indicated. For details, see table 2.

tures, the high-pressure limit is given by P = 8000 + 13 T, so far as these points alone can define it.

A closer determination may be obtained from the runs in which the starting material was synthetic glass of jadeite composition. Crystallization of this glass takes place more readily than does recrystallization of the minerals, and X-ray patterns indicating crystalline phases were obtained in nearly all cases. The amount of crystallization is sensitive to catalytic action, however, the best results being obtained with unsealed capsules containing initially about 15 percent of gibbsite which breaks down at a moderately high temperature to corundum and water. Free water was introduced on a number of occasions but, unless the capsules were sealed, it was probably lost too soon to be of value; if sealed in, on the other hand, very small amounts of water were sufficient to produce a low-melting silicate-water melt or solution which, on quenching, yielded only glass. It is assumed that water does not enter into the composition of the crystalline phases and, consequently, that the position of the equilibrium curve is not affected by its presence. At temperatures below about 600°C, however, analcite may be formed, and water becomes a true component in the reactions, analcite = jadeite plus water, and analcite = albite plus nepheline plus water.



Fig. 5. Transformation of synthetic glass of jadeite composition. The line marked "theoretical" is the equilibrium curve for the reaction, ab + ne = 2 jd, according to the calculations of Kelley et al. (1953). For details, see table 2.

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The results for the runs in which glass was the starting material are plotted in figure 5, according to the crystalline phases identified after quenching from the indicated pressures and temperatures. In addition to the cases in which only jadeite, or only albite and nepheline (and corundum, when gibbsite was used) could be distinguished, there are a number of instances where jadeite, albite, and nepheline were found together; with one or two exceptions, these were cases where no catalyst had been added, or where only water had been added and had probably been lost. Nearly all of the corresponding points lie in the jadeite field, as already established by the reaction of mineral albite and nepheline. It seems probable that the transformation of the glass to crystalline jadeite passes through a stage of metastable crystalline albite plus nepheline and that, if the reaction is not sufficiently rapid, the quenched material shows both phases. Of the runs with gibbsite, only one (no. 35) shows this effect. If this explanation is correct, then we may consider that all of the runs which show crystalline jadeite in the product lie in the jadeite field. The equilibrium line is then fixed within relatively narrow limits; the best graphical solution falls close to the line, P = 1000 + 18.5T. The intercept at $T = 0^{\circ}C$, found by linear extrapolation, is subject to an uncertainty of perhaps $\pm 1000 \text{ kg/cm}^2$; the position is best determined in the neighborhood of 900°C to 1000°C, where the uncertainty may be several hundred bars, or about 20 degrees, and there are no useful points below about



Fig. 6. Transformation of natural analcite and synthesis of analcite. For details, see table 2.

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600°C. The uncertainty of the slope is about ± 1 bar/deg. Presumably, in the absence of water, the portion of the equilibrium line below 600°C could be realized given sufficient time or suitable non-reacting catalysts.

Additional support for this line is given by the experiments in which the starting material was natural analcite. The results are plotted separately in figure 6. Three regions may be distinguished: in the first, analcite breaks down to albite plus nepheline, with the albite lines usually much the stronger in the diffractometer pattern; in the second, jadeite appears along with albite and possibly nepheline; finally, in the third region, below 600°C, analcite is unchanged, while either jadeite plus water, jadeite glass plus water, or albite plus nepheline plus water, may be transformed to analcite. The first region is evidently consistent with the (ab + ne) field already found: the second is consistent with the jadeite field already found, but it appears that the breakdown of analcite, like the crystallization of the glass, may pass through a metastable phase of ab + ne. In the jadeite field, this in turn begins to transform to jadeite, and thus these runs may also be used to narrow the region of uncertainty of the equilibrium line. The third field, in which analcite is stable, has been little studied in the present work, but has been outlined by Griggs, Kennedy, and Fyfe (1955a; 1955b.) The equilibrium between analcite and albite plus nepheline plus water has also been investigated by Yoder (1954.) It should be noted that in the present work the reported pressure is the total pressure; the partial pressure of water is not usually known.

The observations are summarized in table 2. Charges showing no change have not been listed. Phases showing only relatively weak lines have been distinguished by parentheses. The uncertainties assigned to the pressures indicate the range of variation of pressure during the exposure to high temperature; the absolute pressures are subject to the errors discussed above. The temperatures include the uncertainty arising from temperature gradients as well as fluctuations during the run but are also subject to additional errors of absolute value. Many of these runs are for conditions well removed from the boundary and contribute little to the determination of its position, except as part of the process of narrowing down the limits. Only those closest to the boundary have been plotted in figure 5. The point given by Coes (1955) as representing the "best conditions" for the formation of jadeite, at 900°C and 20,000 bars, is indicated by a cross; this point lies well within the jadeite field as determined by the present work, about 2000 bars above the equilibrium pressure for 900°C.

Dry charges of natural jadeite and of albite plus nepheline were melted on two occasions to give some preliminary information on the liquidus relations at high pressure. In the first, the pressure was 21,350 kg/cm²; the temperature was first held at 1280°C, then lowered to 1190°C and held for 20 minutes, then quenched. Albite and nepheline formed from the glass made from the natural jadeite; the ab + ne mixture was still all glass. Accordingly, the higher temperature has been plotted in the liquid field, the lower in the ab + ne field. In the second case, on quenching from 1350°C and 25,100 kg/cm², the capsules, filled as before, contained only glass; and hence this point has been plotted in the liquid field. Dry natural jadeite did not melt

		Su	mmary of Ex Abbr	perimental Res eviations	ults
	ab- ana co- gi-	—albite a—analcite —corundum —gibbsite		jd—jadeite jd gl—jadeite gla ne—nepheline wa—water (S)—sealed capsu	ss ule
Run	Time hours	Pressure kg/cm ²	${\stackrel{\rm remperature}{\stackrel{\circ}{C}}}$	Charge	Crystalline products
77	2.0	$9,000 \pm 30$	535 ± 15	id + wa (S)	jd + (ana)
75	1.4	$9,\!350\pm30$	610 ± 10	ana jd + wa	$ab + ne \\ ab + ne + ana$
72	2.0	$10,\!300\pm100$	500 ± 10	ab + ne + wa	ana + ab + ne
71	1.6	$10,\!700\pm\!50$	630 ± 10	ana (S)	ab + ne
80	1.5	$12,\!000\pm\!30$	575 ± 35	jd gl + wa	ana
20	2.0	$12,200 \pm 200$	775 ± 25	jd gl + NaF	(ab) + ne
49	1.5	$12,\!400\pm\!100$	1015 ± 30	jd gl	ab + ne
96	3.5	$12,\!700\pm\!200$	610 ± 20	$\mathrm{jd}\mathrm{gl}+\mathrm{gi}$	ab + ne
53	1.3	$12,\!800\pm100$	1050 ± 25	jd	jd + ab + ne
54	0.8	$12,\!800\pm\!100$	1025 ± 20	jd jd gl	jd + ab + ne ab + ne
74	2.0	$13,\!400\pm\!50$	525 ± 15	ana	jd + ab
21	1.0	$13,\!300\pm\!300$	675 ± 25	ana jd gl + gi (S)	ab + ne ab + ne
24	1.4	13,000±300	775 ± 25	$egin{array}{l} { m jd} { m gl} + { m NaF} \ { m jd} + { m gi} \ { m ana} \ { m jd} { m gl} + { m gi} \end{array}$	(ab) + ne (jd) + ab + ne + (co) ab ab + ne + (co)
70	1.7	$14,\!000\pm\!50$	610 ± 10	ana	jd + ab + (ne?)
25	3.0	$13,900 \pm 500$	750 ± 50	jd gl + gi jd + gi ana	ab + (co) + (gi) jd + (ab) jd + ab + (ne?)
63	1.5	$15,400 \pm 100$	825 ± 25	jd gl + wa jd + wa ana	ab + ne jd + ab + (ne) ab + ne
67	1.6	$15,700 \pm 100$	615 ± 10	ana	jd + ab + (ne)
			600 ± 10	ana (S) jd gl + wa ab + ne + wa	jd + ab + (ne) jd + (ab + ne) jd + ab + ne
60	2.0	$15,\!850\pm50$	825 ± 10	ana	ab + (ne)
61	2.0	$16,\!100\pm\!100$	825 ± 10	ana jd gl + wa	ab + ne + jd ab + ne + jd
69	0.5	$16,200 \pm 200$	1150 ± 20	jd gl jd	$ab + ne \\ jd + ab + ne$
59	2.3	$16{,}500{\pm}100$	815 ± 15	ana	jd + ab + (ne)
32	1.5	$16,\!700\pm100$	950 ± 20	jd gl + gi (S)	ab + ne + co
45	1.8	$16,700 \pm 200$	$875\pm\!15$	jd gl (S)	ne + (ab)
58	1.5	$18,000 \pm 300$	920 ± 20	jd gl	ab + ne

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Run	Time hours	Pressure kg/cm ²	Temperature °C	Charge	Crystalline products
18	2.5	$18,300 \pm 200$	$775\!\pm\!25$	jd gl + gi jd gl + NaF	$\operatorname{jd}_{\operatorname{jd}}$ + co
34	1.5	$18,\!300\pm\!200$	840 ± 60	jd gl + gi (S) ana (S)	jd + co jd + ab + (ne)
35	1.5	$19,\!000\pm\!50$	950 ± 20	jd gl + gi (S) ana (S)	jd + co + ab ab + (jd + ne)
36	1.5	$19,200 \pm 200$	950 ± 20	ana (S)	jd + ab + (ne)
57	2.0	$19,\!400\pm\!50$	935 ± 30	jd gl ana	$_{jd}^{jd}$ + ab + (ne?)
28	1.0	$19,\!450\pm50$	920 ± 20	jd gl + gi (S) ana (S)	jd + co jd + ab + (ne)
38	1.5	$19{,}500\pm50$	975 ± 25	jd gl + gi (S) jd gl + wa (S)	jd + co (ab) + ne
40	1.0	$19,\!000\pm\!500$	1000 ± 100	$\mathop{\mathrm{jd}}_{\mathrm{jd}} \mathop{\mathrm{gl}}_{\mathrm{gl}} + \mathop{\mathrm{gi}}_{\mathrm{l}}$ (S)	(ab + co) ab + ne
44	1.5	$19,400 \pm 300$	1000 ± 25	jd gl (S) jd gl + wa	ab + ne (ab)
30	1.4	$19,\!200\pm700$	900 ± 20	jd gl + gi (S) ana (S)	jd + (co) jd + ab
43	1.0	19,300±600	1000 ± 50	jd gl + wa jd gl	ab + ne ab + ne
37	1.5	$19{,}600{\pm}400$	950 ± 20	jd gl + gi (S)	jd + co
65	1.5	$20,\!100\pm\!100$	$\begin{array}{c} 1035 \pm 15 \\ 1080 \pm 20 \end{array}$	jd gl + wa jd + wa	$ab + ne \\ jd + ab + (ne)$
46	1.5	$21,\!250\pm50$	1020 ± 10	jd gl (S)	ab + ne + (jd)
56	1.3	$21,\!350\pm350$	1055 ± 25	jd gl ab + ne	jd + ab + ne jd + ab + ne
81	0.3	$21,\!350\pm\!50$	1190 ± 25	jd + wa	ab + (ne)
48	1.9	$21,\!800\pm\!200$	995 ± 10	jd gl	jd + ab + ne
31	2.0	$21,200 \pm 800$	900 ± 20	jd gl + gi (S) ana (S)	jd + ab + (ne)
66	1.4	$23,900 \pm 30$	1080 ± 50	jd gl + wa jd gl ana	jd + ab + ne jd + ab + ne jd + (ab)
68	1.4	$25,500 \pm 100$	1175 ± 50	ab + ne jd gl jd	ab + ne + jd jd + (ab) jd (not melted)
55	0.1	$26,000 \pm 50$	1085 ± 30	jd gl ab + ne	jd + ab + ne ab + ne + (jd)

TABLE 2 (Continued)

in 1.4 hours at 1175° and $25,500 \text{ kg/cm}^2$. The very tentative construction of the liquidus and solidus curves in figure 5 is based on these results, plus those for one atmosphere given by Greig and Barth (1938.)

The melting relations with water at high pressures remain to be worked out. The results with sealed capsules indicate reductions of melting point of several hundred degrees, but the water content has not been determined. A

beginning has been reported by MacKenzie (1954) for water pressures up to 1000 bars.

In many of the runs listed in table 2, capsules were included with charges having compositions of other systems, such as kyanite and pyrope. Both of these minerals have been crystallized, but further work is required for the delineation of their fields of stability.

DISCUSSION

Thermochemical considerations.—The thermodynamic properties of jadeite, nepheline, and albite are, for silicates, exceptionally well known. A comparison of the equilibrium relations derived from thermochemical data with the experimental results is useful in several ways. First, the theoretical relations refer to equilibrium conditions, while the experimental curve is derived from short-time experiments in which equilibrium may not have been reached. The equilibrium curve calculated by Kelley and others (1953) is shown in figure 5. The agreement with the experimental curve, probably within the uncertainties of the two sets of data, suggests that a fairly close approach to equilibrium has been attained in the experiments.

In the second place, the experimental curve can be used to improve the thermochemical data, and thus to reduce the uncertainty in calculating the phase boundaries in other reactions involving albite, nepheline, and jadeite. The slope of the equilibrium curve is given by $dP/dT = \Delta S/\Delta V$, where ΔS is the difference in entropy between the products and the reactants, ΔV the difference in volume. Kelley and others (1953) calculate a slope of 20 bars/deg; MacDonald (ms), in a critical review of the data, gives 20 ± 3 bars/deg. The required data are shown in table 3. These values are in such close agreement with the experimental value of 18 ± 1 bars/deg that we cannot improve the values for ΔS or ΔV . It should be noted that, though in general dP/dT is a function of T (or of P) and the phase boundaries should show curvature, in the present study they are assumed to be straight. Neither the thermochemical nor the experimental data are of sufficient accuracy to show minor changes of slope of the equilibrium line, but both sets rule out changes greater than about 5 bars/deg for temperatures below 1200°C.

Phase	Composition	Entropy cal/deg mole	Volume cm ³ /mole		
α-quartz	SiO_2	10.0 ± 0.1	22.64 ± 0.03		
nepheline	NaAlSiO ₄	29.7 ± 0.3	54.2 ± 0.5		
jadeite	NaAlSi ₂ O ₆	31.9 ± 0.5	60.7 ± 0.6		
albite	NaAlSi ₃ O ₈	50.2 ± 0.5	$100.8 \hspace{0.2cm} \pm \hspace{0.2cm} 1.0 \hspace{0.2cm}$		

TABLE 3								
Entropies	and	Volumes,	with	Estimated	Uncertainties			

The position of the equilibrium line depends upon the heat of reaction ΔH , the equation of the line being $\Delta G(T, P) = \Delta H - T\Delta S = 0$, where G is the Gibbs potential. Table 4 shows the values of the heat of reaction for ab + ne = 2jd, according to the sources of the materials. The heat of this reaction is not measured directly but is obtained as a difference involving three relatively large numbers, the heats of solution of the three minerals.

Errors of 2-3 percent in the heats of solution could account for the whole range of values of Δ H.

The calculations of Kelley and others (1953) depend upon the selection of $\Delta H = -5.5$ kcal/mole, corresponding to the values for Varuträsk albite and Burmese jadeite; these are also the materials which they used in their studies of heat capacity. If we take the equilibrium pressure for the ab + ne= 2jd reaction, at 25°C, to be 1500 bars as found by extrapolation of the experimental line, we obtain $\Delta H = -3.6 \pm 0.8$ kcal/mole, for this temperature. Though lower than the average, and lower than the value adopted by Kelley and others, this is within the range given by Kracek and others (1951) and is probably not seriously inconsistent with their values.

(Kracek, Neuvonen, and Burley, 1951)							
Albite	Nepheline	Jadeite	∆H kcal/mole				
Varuträsk	Synthetic	Burma	-5.5				
Varuträsk	22	Japan, ground in agate mortar	-6.7				
Varuträsk	"	Japan, ground in mullite mortar	-3.6				
Amelia	22	Burma	-7.2				
Amelia	22	Japan, ground in agate mortar	-8.4				
Amelia	77	Japan, ground in mullite mortar	-5.3				

TABLE 4									
Heat of	Reactio	n, ab	+ n	e =	2jd,	at !	25°C,	1	bar
	(Kracek	Neuvo	non	and	Burley	7 1	051)		

With this value, a revised calculation may be made for the reaction, albite = jadeite + quartz, which has been considered by Kracek and others (1951) and by Kelley and others (1953.) From the data of table 3, the slope of the equilibrium line is found to be 20 ± 4 bars/deg. Let us suppose that the heat of the reaction, ab + ne = 2jd, is -3.6 ± 0.8 kcal/mole and that some or all of the heats of solution for albite, nepheline, and jadeite are in error. If all of the error is attributed to the jadeite heat of solution, then the heat of reaction for ab = jd + qu becomes +1.0 kcal/mole. If all of the error is attributed to the heat of solution of albite, then the heat of reaction becomes +1.9 kcal/mole. If we take a mean value, $\pm 1.5 \pm 2$ kcal/mole, the equilibrium curve for the breakdown of albite to jadeite plus quartz is given by $P = 9000 \ (\pm 5000) \ + \ 20 \ (\pm 4)$ T, with P in bars, T in degrees centigrade. It is perhaps worth remarking that jadeite cannot be formed from nepheline plus quartz at relatively low pressures, as seems to be suggested by Kelley et al. In a mixture having the composition of jadeite, nepheline and quartz first react to form albite, according to ne + 2 qu = ab (Reaction C of Kracek et al.) at all points in the ab + ne field of figure 5. The albite will then react with the remaining nepheline to form jadeite only in the jadeite field. The reaction of nepheline and quartz to form albite was observed a number of times in the course of these experiments, but in only one case (no. 61) did the reaction proceed far enough to produce jadeite. It is probably more advantageous to begin with albite and nepheline, to avoid the additional reaction.

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Fig. 7. Theoretical temperature-pressure relations in the plane of (dry) albite composition.

The P-T relations in the plane of albite composition are shown in figure 7. At pressures somewhat above those of the albite breakdown, the quartz transforms to a high-density polymorph, "coesite" (Coes, 1953; MacDonald, unpublished). The slope of the albite melting curve has been computed from the change of entropy on melting (Kracek and Neuvonen, 1952) and the volume change (Goranson, 1938) as 40 bars/deg or 25° /kilobar; the uncertainty may be as large as ± 40 percent.

It is interesting to attempt the construction of temperature-composition planes at various pressures for the system NaAlSiO4-NaAlSi3O8 on the basis of the two P-T diagrams (figs. 5 and 7) of constant composition. Figure 8a shows the relations at one atmosphere as determined by Greig and Barth (1938.) Possible forms of the temperature-composition relations at 15,000 bars and at 30,000 bars are shown in figure 8b and 8c. The liquidus relations are largely hypothetical but are somewhat controlled by the preliminary results of melting of material of jadeitic composition at 25,000 bars, and by the estimated increase of melting temperature of albite already cited. We have no experimental results as yet on the behavior of NaAlSiO₄ at high pressures; it seems likely, however, that nepheline will either break down to two or more phases of high density or transform to a high-density polymorph, indicated as nepheline - II in figure 8b and 8c. The possibility of such a form, having an olivine structure, is suggested by the relations in the system CaMgSi₂O₆— NaAlSiO₄—SiO₂, for which a preliminary diagram by Schairer is given by Yoder (1950b, p. 318).³

³ Since the construction of figure 8, evidence for a transformation of nepheline at high pressures has been found by Mr. F. R. Boyd, Jr. at the Geophysical Laboratory.



Fig. 8. The binary system, NaAlSiO₄---NaAlSi₃O₅, at several pressures. The diagram at 1 bar after Greig and Barth (1938). Liquidus relations largely hypothetical.

Certain features of the postulated liquidus relations require comment. The eutectic is shown as moving toward the NaAlSiO₄ end of the system; this is suggested by the rapid increase of melting point of albite, but the amount of displacement is unknown. It is quite possible that an albite plus liquid field should be indicated in figure 5, and that the eutectic, at 15,000 bars, has passed to the nepheline side of the jadeite composition. The ab + ne = 2jd equilibrium curve must reach a melting curve somewhere in the region indicated. We have supposed that beyond about 25,000 bars, jadeite melts congruently; this again requires verification.

The significant feature illustrated in figure 8 is the reduction of the fields of stability of albite and nepheline. At 1 bar these minerals are stable from ordinary temperatures up to about 1000°C. At 30,000 bars the assemblage albite plus nepheline is nowhere stable; the minerals nepheline and albite are stable only in the presence of jadite or liquid, except possibly for compositions near the end points at temperatures close to melting.

Geologic considerations.—In applying these results to the Earth, a major restriction must be kept in mind. Only the system $NaAlSiO_4$ — $NaAlSi_3O_8$ has been studied, and very few rocks can be adequately described in terms of these two components. The inferred albite breakdown, which would not be affected by the presence of excess silica, is applicable to a larger number of visible rock types. We probably do obtain, however, maximum pressures and roughly maximum depths at which various types of rock may have originated. When these observations are compared with estimates of internal temperatures, certain speculations as to the nature of the Mohorovičić discontinuity begin to assume a new plausibility.

Only a few natural occurrences of relatively pure jadeite have been described; besides those reported by Yoder (1950b), there are several new localities (Yoder and Chesterman, 1951; Wolfe, 1955). One of the classic localities in upper Burma has jadeite in association with albite, or nepheline, or both (Yoder, 1950b, p. 237). Our results indicate temperatures of crystal-

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lization of 400-700°C if the pressure were 15,000 bars (with lower temperatures for lower pressures) in order to explain the jadeite-albite assemblage. Similiarly, high pressures and relatively low temperatures would be required for the albite-jadeite-quartz assemblage found in Japan (Yoder, 1950b, p. 240).

The nepheline-albite assemblage is common in nepheline syenites. Both minerals, as found in nature, are in the form of complex solid solutions. The nephelines of plutonic rocks contain KAlSiO4, SiO2, and CaAl2Si2O8 in addition to NaAlSiO₄ (Miyashiro, 1951.) The feldspar may contain appreciable amounts of KAlSi₃O₈ and CaAl₂Si₂O₈ in addition to NaAlSi₃O₈. In order to discuss the stability of complex solid solutions at high pressures, we require data on excess volumes and excess enthalpies. MacDonald (ms) shows that an alkali feldspar containing both NaAlSi₃O₈ and KAlSi₃O₈ will break down to jadeite plus orthoclase and quartz at lower pressures than those at which pure albite will break down. A similar effect may be anticipated in the case of other components than NaAlSiO4 in nepheline. The experimental curve of figure 5 would then fix an upper limit for the pressure at which nepheline syenites could have formed, and with the liquidus would define a pressuretemperature region for formation of nepheline syenites. In nature this region would become more restricted, since the liquidus would be lowered by other components, especially water, and the equilibrium curve would be shifted toward lower pressures.

In the same way, the line for the reaction, ab = jd + qu, fixes maximum pressures (with due regard for the large uncertainty) for the formation of alkali feldspar or alkali feldspar-quartz assemblages. Such abundant rocks as granites and granodiorites probably crystallized at pressures well below those for this reaction.

Ectogites present a more complicated problem. The pyroxene "omphacite" in eclogite is generally a complex solution of such components as Ca(MgFe) Si₂O₆, NaFeSi₂O₆, and NaAlSi₂O₆. Since diopside, hedenbergite, and acmite are stable at all temperatures up to the melting points at 1 bar, it is probable that the pressure needed to form omphacite is lower than the pressure needed to form jadeite. The pressures required to form an omphacite pyroxene in an eclogite undersaturated with SiO₂ would be lower, perhaps much lower, than those for the reaction ab + ne = 2jd; the omphacites in quartz-bearing eclogites would require pressures no greater than those for the reaction ab = jd + qu. It seems likely that, above some moderate pressure, there will be continuous solid solution between diopside and jadeite.

The considerations reviewed above bear on the general problem of the stability within the Earth of the feldspars and feldspathoids. While it seems clear that these minerals must become unstable at depths of the order of some tens of kilometers, the discussion is complicated by the circumstance that we must consider multicomponent systems and by the uncertainty of the temperature-pressure relations in and below the crust. Several estimates of temperature versus depth (Poldervaart, 1955, p. 113) are shown in figure 9, together with the equilibrium curves which we have been considering. The line, P = 1000 + 18.5T for the ab + ne = 2jd equilibrium, has been trans-



Fig. 9. Equilibrium curves for several reactions versus depth, and estimated temperature-depth curves. A, B, and C represent different estimates for average continental conditions; D is an estimate for temperatures below average ocean of 4-km depth. The quartz inversion after Yoder (1950a), the quartz-coesite curve after MacDonald (1956).

formed to a temperature-depth curve, on the usual heavy-liquid assumption; in the typical continental section, the density has been taken as 2.8 to a depth of 33 km, 3.3 for greater depths. The line for the reaction, ab = jd + quhas also been drawn, as well as the quartz-coesite line, after MacDonald (1956) and the α - β -quartz curve, after Yoder (1950a). The curve of lowest temperature (A) corresponds to an extreme concentration of heat sources within the crust; it intersects the jadeite curve at about 12 km. Curve B, a more reasonable distribution, is based on the assumption that one-half of the surface heat flow originates below the crust; this intersects the jadeite curve at about 40 km. Curve C of the reference, intended to give an upper limit for a crust of normal thickness, might intersect the jadeite curve at some depth greater than 50 km, depending upon further assumptions about conductivity at depth and distribution of heat sources.

Estimates for a typical oceanic section are shown in the small corner insert; the temperatures correspond to Case D of the reference, and the jadeite equilibrium line has been transformed to correspond to a structure composed of 4 km of water, 6 km of rock of density 2.8, with a density of 3.3 thereafter. With these temperatures, points above a depth of about 37 km would lie in the albite-nepheline field, and the discontinuity at about 10 km below sea level could not be accounted for by the simple jadeite transformation. With allowance for additional components, however, the transformation will

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probably shift to lower pressures, and none of these numbers should be regarded as finally disposing of the matter.

Whether or not it proves possible to account for the Mohorovičić discontinuity in these terms, it seems safe to conclude that quartz, the feldspars, and the feldspathoids would transform to high-density forms at relatively moderate depths in the Earth. From the known properties of jadeite and garnets, we may conclude that these high-density forms would have elastic properties close to those of olivines and orthopyroxenes. The implications for geochemistry and petrology, and for our understanding of the structure and evolution of the Earth, are far-reaching.

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