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MELTING RELATIONS IN THE SYSTEM JADEITE–DIOPSIDE AT 30 AND 40 KILOBARS

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ABSTRACT. At 30 kb and 40 kb jadeite–diopside is a binary system. A melting interval extends for the full compositional range and is analogous to that observed in plagioclase feldspars. This system leads to petrogeny's residua system, and the fractionation behavior follows Bowen's trend except that an extremely narrow melting interval may produce only limited concentrations of jadeite constituents in high-pressure magmas.

Relationships in the subsolidus region can be deduced in a qualitative way from volumetric data measured on solid solutions along the binary join. Calculations of a regular solution model suggest that the addition of diopside to jadeite will not have a great effect on the breakdown of jadeite to albite + nepheline.

INTRODUCTION

The pyroxene omphacite is mainly a solid solution of jadeite ($NaAlSi_2O_6$)–diopside ($CaMgSi_2O_6$). The occurrences of omphacite are intriguing because of its most common association with high-pressure minerals such as pyropic garnet, kyanite, and diamond. The natural environment of many omphacites, therefore, is in the high-pressure zone of the Earth's crust and mantle.

Laboratory observations of systems containing the omphacite composition have heretofore been limited to plagioclase, nepheline, and diopside, phases stable under the low-pressure conditions of the upper crust. It has been the purpose of the present study to continue some of these investigations at high pressures which are more consistent with the geologic setting of the mineral phases involved.

Bowen's (1913) classic experiments on melting phenomena proved the exact relationship of the melting interval in the Ab($NaAlSi_3O_8$)–An($CaAl_2Si_2O_8$) system which previously had been investigated at the U. S. Geological Survey and the Geophysical Laboratory (Day and Allen, 1905). His analysis of the actual two-phase melting region revealed the process of fractional crystallization by which natural melting produces zoned and reversed zoned plagioclase crystals. This process accounts for the existence of a nearly continuous variation of the compositional phase region in many igneous plagioclases. After this study on plagioclase, Bowen in collaboration with Schairer continued studying melting phenomena and, in particular, investigated systems containing FeO, K_2O, and MgO in addition to the plagioclase components (for example, Bowen, 1915). Bowen (1937) assembled much of his and Schairer's phase equilibrium results and with great insight proposed petrogeny's residua system. This system, including mainly $NaAlSiO_4$–$KAlSiO_4$–SiO_2, was the goal of the crystal fractionation process containing the components SiO_2–Al_2O_3–FeO–CaO–MgO–Na_2O–K_2O, which includes about 97 percent of the average igneous rocks (Bowen, 1937). Phases containing much of the CaO

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and MgO are precipitated in the course of the fractionation trend, and the liquid is therefore enriched in alkalies, alumina, and silica. Further experimentation and field observation have frequently borne out Bowen's contention.

Attempts to define the exact nature of the liquid residue within the alkali–alumina–silicate ternary have been rewarding. In following many of the same chemical systems as Bowen, Schairer and Yoder obtained additional information on petrogeny's residua system. Experimentally following the trends within the 7-component system (a summary of relevant diagrams is given in Yoder and Tilley, 1962, p. 399), Schairer and Yoder (1960) showed that residual liquids fall within the zone suggested by Bowen but separated into two groups within the zone. This separation is caused by the development of a thermal divide, for example, along the albite–diopside join. On one side of the divide the system is undersaturated in SiO_2, and a nepheline normative trend is produced. On the other side of the divide the system is supersaturated with SiO_2, and a quartz normative trend is produced. Evidently igneous liquids can follow either trend depending on slight differences in original composition and the fractionation process. The residua system is the final goal of most igneous processes and therefore is of utmost importance in interpreting the geology of rocks exposed at the Earth's surface.

The fractionation process originates at great depths and therefore at high pressures within the Earth's crust and mantle. The basic question is how does high-pressure behavior modify the trends at depth that lead to the various portions (oversaturated, saturated, undersaturated) of petrogeny's residua system at low pressure? Jadeite–diopside lies in the system nepheline–diopside–quartz, and a study of its melting relations at high pressure should provide a partial answer to the nature of the trend determining processes.

OMPHACITE COMPONENTS

The usual significance of albite as excluding nepheline ($NaAlSiO_4$) and quartz (SiO_2) compatibility ceases to be meaningful at high pressures. Jadeite, silica-poor compared to albite, becomes more stable and constitutes a member of a new thermal divide. Jadeite-diopside at high pressure may be thought, therefore, to play a corresponding role as albite-diopside at low pressure. In another analogy, the jadeite-diopside join might be considered to act as a thermal divide at high pressure as the plagioclase join does at low pressure because jadeite, not albite, is stable.

Liquidus relationships were first investigated at 30 kb because past experience with jadeite melting (Bell, 1964; Bell and Roseboom, 1965) demonstrates this to be the lower pressure limit of congruent behavior. Relationships at 40 kb were investigated next in order to examine pressure effects and at the same time to support the phase equilibria analysis of the 30 kb section. Temperatures required at 40 kb are considerably higher, and therefore sluggish melting, which is characteristic of sodium-bearing silicates, is nearly eliminated. Subsolidus relationships were not

examined experimentally; however, it is possible to make some predictions on the basis of the present results.

It should be pointed out that significant components of natural omphacite other than jadeite and diopside are acmite ($NaFe^{+3}Si_2O_6$) and Tschermak's molecules ($CaAl_2SiO_6$, in particular). Acmite is the most important, being present commonly in amounts up to about 10 wt percent (Coleman and others, 1965). It is assumed in the initial experimental studies that neglecting components other than jadeite and diopside will not greatly affect the results. Actually there may be a stronger effect than supposed although some evidence in the subsolidus region seems contrary to this suggestion. A few experiments on the breakdown of natural omphacites containing acmite by Newton and Smith (1967) support this view. This particular aspect will be discussed below.

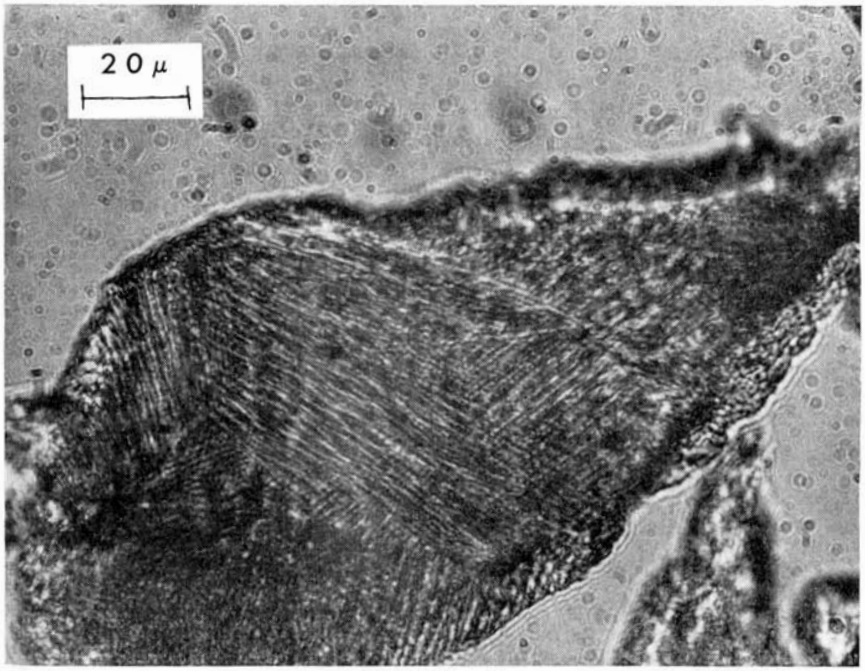
EXPERIMENTAL TECHNIQUES AND ANALYSIS

A single-stage, solid-media apparatus (Boyd and England, 1960) was employed to generate the necessary temperature and pressure conditions. The latest techniques with this apparatus (Bell and England, 1967) were used to minimize frictional and other pressure errors. The uncertainty in pressure is now believed to be $\pm$ 1 kb and and in temperature, $\pm$ 10°C. The starting materials, glasses made available for the study by Dr. J. Frank Schairer, are the same preparations used by Schairer in his experiments in the system nepheline–diopside–silica (Schairer and Yoder, 1960). High-pressure crystalline assemblages of compositions along the jadeite–diopside join were synthesized in batches of 300 to 500 mg. Runs to determine the phase relations were made by raising the glass or crystalline assemblage to pressure and temperature and then quenching.

Two types of problems were encountered. One of these is the quenching behavior of jadeite–diopside compositions. Diopside solid solutions melt and crystallize rapidly at the solidus and liquidus; however, a liquid cannot be quenched to a glass near the melting temperatures. Quench crystals with a feathery appearance, such as those shown in plate 1, are used to establish the liquid field. After some experience "liquids" and crystals along the join can be identified with precision. Microscopic examination is mainly limited to the recognition of textures, since the small grain sizes rarely permit optical measurements. Difficulties in interpretation arise at the jadeite-rich compositions because these do not produce feathery quench crystals. At intermediate compositions the quench crystals change their appearance to a fine-grained interlocking aggregate. At compositions more jadeite-rich than 50:50 wt percent, glass, not quench crystals, is observed, and the problem of sluggish melting is encountered. At temperatures below 1400° runs of at least 1 hour are necessary to melt jadeite-rich compositions, and about the same length of time is required to crystallize a jadeite-rich liquid. In contrast, melting occurs in 5 to 15 minutes with diopside-rich compositions.

The second and perhaps more difficult problem arises with jadeite-rich compositions because of the effect of water on melting. Even the

PLATE 1



Quench crystal: $Di_{85}Jd_{15}$, plane polarized.

slightest amount of water will lower the melting by several hundred degrees. The procedure followed was to heat together the starting materials and the furnace parts in a stream of nitrogen at 800° to 900°C for 30 minutes immediately prior to the run. It was necessary to introduce the sample and furnace parts while still hotter than 100°C into the apparatus to establish reproducibility. No crystalline products were produced during the drying process.

Powder X-ray diffraction was used for identification and accurate characterization of the phases. Unit cell volumes of crystalline phases in the join were measured by use of cell parameters obtained by means of a Norelco diffractometer. Calibration depended on an internal standard which was a specially annealed batch of NaF prepared by Dr. Brian Skinner. Dr. Charles W. Burnham assembled the data for a least-squares volume refinement program which he has written in Fortran IV for the IBM-7094 computer. A solid solution of 50:50 wt percent was measured and computed for independent comparison with natural omphacite by Dr. J. J. Papike of the U. S. Geological Survey.

Experimental products were subjected to additional examination with an Applied Research Laboratory model EMX electron microprobe, made available at the Goddard Space Flight Center. Crystals could not be analyzed as individuals due to the small dimensions (usually less than

5 μ) so only bulk analysis could be made. There was no indication either from X-ray diffraction or microscopic examination that more than one crystalline phase was present. The main purpose of the microprobe analysis was to compare the melting interval compositions with those deduced from the temperature-composition diagram by analyzing the composition of glass in equilibrium with crystal.

The usual problem of sodium loss in probe analyses was eliminated by counting sodium at various time intervals and extrapolating back to zero time. Sodium, magnesium, aluminum, silicon, and calcium were analyzed using the initial glass preparations as standards. It was not necessary to apply corrections for the matrix, and the resulting compositions agreed within 0.5 percent of those expected from the melting relations.

Temperature-composition sections of 30 kb and 40 kb are given in figures 1 and 2 and the data in table 1. The melting interval is extremely narrow at the jadeite end which makes its detection difficult. The interval is well established at the diopside end, however, and the electron probe measurements provide additional confirmation.

There are obvious similarities and dissimilarities between the melting interval of figures 1 and 2 and that in the plagioclase system. For example, melting occurs over a smaller interval: maximum $\approx$ 40°C for jadeite-diopside at 30 kb; maximum $\approx$ 200°C for plagioclase at 1 atm. Keeping in mind the 20°C uncertainty range of overlap in these experiments (due to the $\pm$ 10°C temperature uncertainty) a small interval is not easily detectable. In order to check the experimentally determined plagioclase interval against thermodynamic theory, Bowen (1913) calculated the liquidus and solidus by assuming ideality of solution and em-

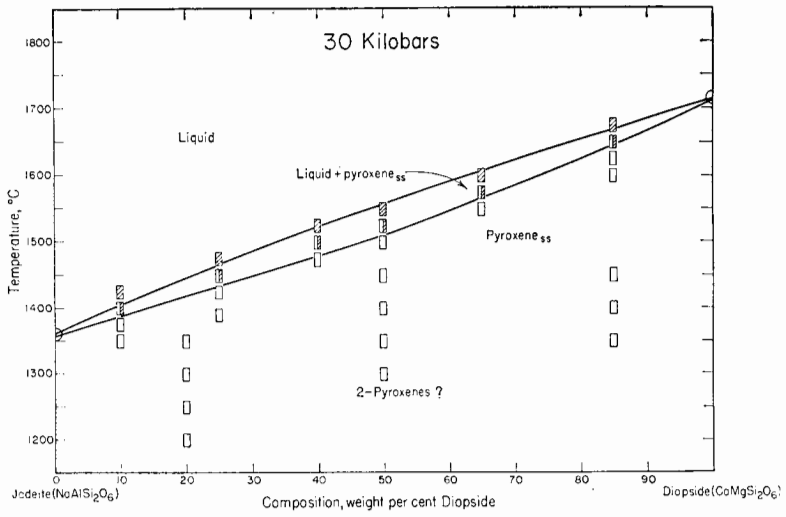


Fig. 1. Temperature-composition section for jadeite-diopside at 30 kb.

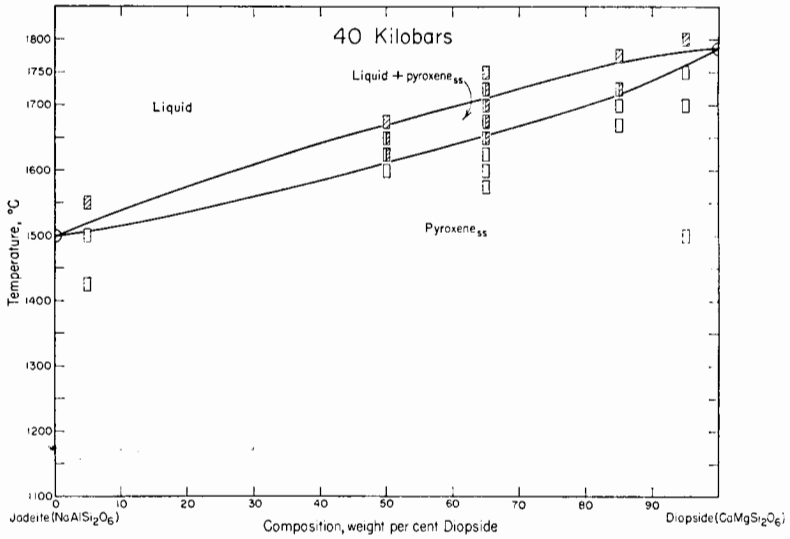


Fig. 2. Temperature-composition section for jadeite-diopside at 40 kb.

ploying the latent heats of melting of the pure end members. Computing the ΔH of fusion for Ab and An across the binary, he was able to support theoretically his most careful experiments by showing the constancy of ΔH within a few hundred calories. These ΔH values have since been documented by calorimetry (Robie and Waldbaum, 1968). Since Bowen and, in particular, Schairer (for example, Schairer, 1950) have laid the ground work for this type of melting experiment, it is interesting to use thermodynamics for a slightly different evaluation. Recent applications of ΔH of reaction by Orville and Greenwood (1965) and by Richardson, Bell, and Gilbert (1968) have been useful for analysis of phase diagrams. For example, the ΔH of fusion, when calculated across a melting interval, is extremely sensitive to the Raoult's law approximation. The following equations have been applied to the curves of figure 1 at various temperatures (T) along the melting interval:

$$\Delta H_A = \left(\ln \frac{xl}{xs}\right)\left(\frac{1}{T_A} - \frac{1}{T}\right)^{-1} R$$

$$\Delta H_B = \left(\ln \frac{1-xl}{1-xs}\right)\left(\frac{1}{T_B} - \frac{1}{T}\right)^{-1} R$$

where

$\Delta H_{A,B}$ = the heats of fusion of components A, B

xl,s = mole fractions of the liquidus and solidus phases of T°K

$T_{A,B}$ = fusion temperature (°K) of end member phases A, B

R = gas constant

TABLE 1

Experimental data

P, kb	T, °C	Composition, wt percent	Time, min.	Results*	P, kb	T, °C	Composition, wt percent	Time, min.	Results*
30	1650	$Di_{85}Jd_{15}$	15	L(Q) + C	30	1400	$Di_{10}Jd_{90}$	60	L(G) + C
30	1625	$Di_{85}Jd_{15}$	15	C	30	1375	$Di_{10}Jd_{90}$	60	L(G) + C
30	1600	$Di_{85}Jd_{15}$	15	C	30	1350	$Di_{10}Jd_{90}$	60	C
30	1500	$Di_{85}Jd_{15}$	90	C	40	1800	$Di_{95}Jd_{5}$	5	L(G + Q)
30	1450	$Di_{85}Jd_{15}$	90	C	40	1750	$Di_{95}Jd_{5}$	5	L(Q) + C
30	1400	$Di_{85}Jd_{15}$	150	C	40	1700	$Di_{95}Jd_{5}$	10	C
30	1350	$Di_{85}Jd_{15}$	90	C	40	1775	$Di_{85}Jd_{15}$	5	L(Q)
30	1600	$Di_{65}Jd_{35}$	15	L(G)	40	1725	$Di_{85}Jd_{15}$	5	L(Q) + C
30	1575	$Di_{65}Jd_{35}$	15	L(G + Q) + C	40	1700	$Di_{85}Jd_{15}$	10	C2
30	1550	$Di_{65}Jd_{35}$	15	C	40	1675	$Di_{85}Jd_{15}$	10	C2
30	1550	$Di_{50}Jd_{50}$	15	L(G)	40	1750	$Di_{65}Jd_{35}$	5	L(G)
30	1525	$Di_{50}Jd_{50}$	15	L(G + Q) + C	40	1725	$Di_{65}Jd_{35}$	5	L(G) + C
30	1500	$Di_{50}Jd_{50}$	20	C	40	1700	$Di_{65}Jd_{35}$	5	L(G) + C
30	1450	$Di_{50}Jd_{50}$	60	C	40	1675	$Di_{65}Jd_{35}$	5	L(G) + C
30	1400	$Di_{50}Jd_{50}$	90	C2	40	1650	$Di_{65}Jd_{35}$	5	L(G) + C
30	1350	$Di_{50}Jd_{50}$	120	C2	40	1625	$Di_{65}Jd_{35}$	5	C2
30	1300	$Di_{50}Jd_{50}$	90	C2	40	1600	$Di_{65}Jd_{35}$	5	C2
30	1525	$Di_{40}Jd_{60}$	15	L(G)	40	1575	$Di_{65}Jd_{35}$	5	C2
30	1500	$Di_{40}Jd_{60}$	15	L(G) + C	40	1675	$Di_{50}Jd_{50}$	60	L(G)
30	1475	$Di_{40}Jd_{60}$	15	L(G) + C	40	1650	$Di_{50}Jd_{50}$	60	L(Q) + C
30	1350	$Di_{20}Jd_{80}$	150	C	40	1625	$Di_{50}Jd_{50}$	30	L(G) + C
30	1300	$Di_{20}Jd_{80}$	90	C	40	1600	$Di_{50}Jd_{50}$	10	C2
30	1250	$Di_{20}Jd_{80}$	90	C	40	1550	$Di_{5}Jd_{95}$	40	L(G)
30	1200	$Di_{20}Jd_{80}$	90	C	40	1500	$Di_{5}Jd_{95}$	50	L(G) + C
30	1450	$Di_{10}Jd_{90}$	60	L(G)	40	1416	$Di_{5}Jd_{95}$	10	C2

*L(Q) = liquid, on the basis of quench crystals; L(G) = liquid, on the basis of glass; C = one crystalline phase; C2 = two crystalline phases, on the basis of split (220) X-ray reflection.

These equations are derived from Raoult's and Clapeyron's equations and contain all of the inherent uncertainties. Figure 3 shows that deviations from Raoult's law are striking, and the overall effect is one of a nearly continual lowering of ΔH for both components from either side to a central minimum. This deviation suggests an excess volume of mixing and excess values for this thermodynamic variable. The theory of "excess functions" in thermodynamics was originally clarified by Hildebrand in 1924 (see Hildebrand, 1964, p. 29-47) and later by Guggenheim (1952, p. 29-87). The slight relative maxima at 1750°C for jadeite and at 1788°C for diopside probably are within the uncertainty of the experiments, and they are probably not suggestive of structural changes.

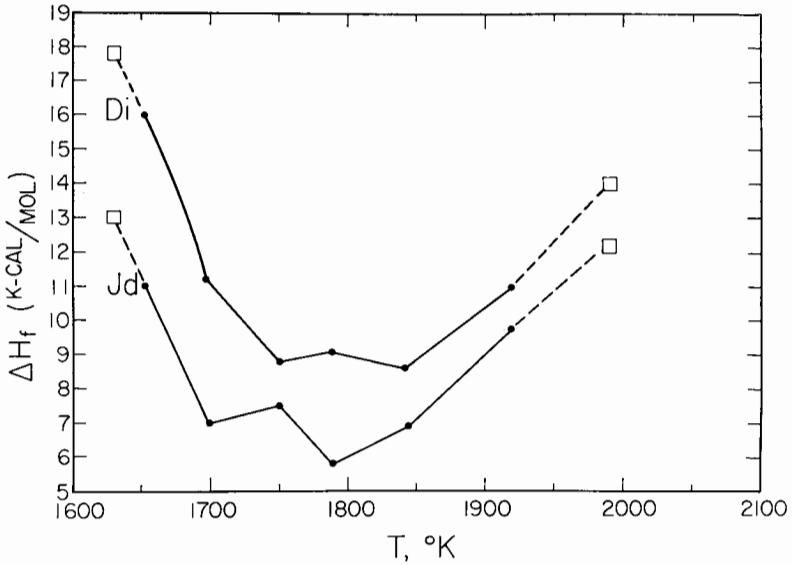


Fig. 3. Heat of melting versus temperature for compositions along the jadeite-diopside join (30 kb).

The first step in attempting to understand the significance of the non-ideality in the jadeite-diopside solid solutions was to measure the unit cell volumes with the highest precision. Values obtained after least squares refinement are listed in table 2, but the effect of compressibility and thermal expansion have not been taken into account. A plot of the volume function can be compared with the linear case of ideality in figure 4. There is a finite excess volume of mixing which is maximized in the central part of the join. Such a large excess volume of mixing suggests a disordered compound which, perhaps, should be expected for phases quenched from high temperatures or for incipiently unmixed phases. Due to the fine grain size (average 4-6 μ) the possibility of a disordered compound cannot be verified by single crystal X-ray diffraction. The observed volume excess makes the possible existence of disorder

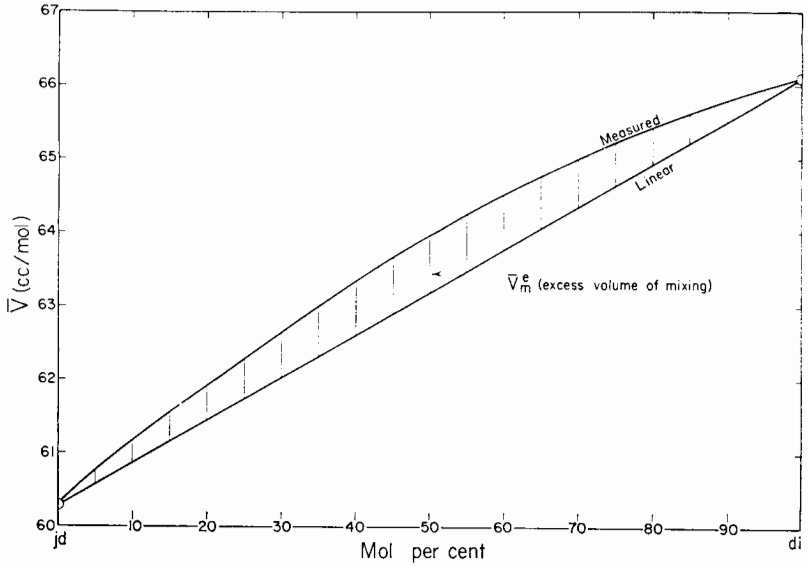


Fig. 4. Molar volumes (30 kb) of jadeite-diopside solid solutions.

TABLE 2

Molar volumes and excess volumes of mixing

for jadeite-diopside solid solutions

Jadeite, mole percent	$\bar{V}$cm^3/mole (measured)	$\bar{V}_m^e$cm^3/mole (measured)	$\bar{V}_m^e$cm^3/mole = $2.56(x_1)(1 - x_1)$
15	...	...	0.325
15.8	65.61	0.355	...
36.0	...	...	0.585
36.8	64.57	0.493	...
50.0	...	...	0.640
51.8	63.88	0.632	...
62.0	...	...	0.590
85.0	...	...	0.325

likely, but disorder would be in contrast with the observation of ordered natural compounds whose compositions lie in the central part of the jadeite-diopside join (Clark and Papike, 1968).

In addition to the problem of order-disorder there is a possibility of compositional unmixing in the jadeite-diopside system. Perhaps it would be of some value to examine the possible criteria for establishing order-disorder and compositional unmixing. First, the phase diagram itself might show the intersection of a phase boundary such as a change in slope of the solidus curve if the order-disorder or compositional unmixing boundary does, in fact, intersect. The present data do not support such an interpretation. Next optical and single-crystal X-ray properties should be unique but cannot be realized because of the fine grain size.

Eventually thermochemical and physical properties might give a positive result, but these have not been attempted. Finally, the information that can be used with the jadeite-diopside compositions is X-ray powder data, including the unit cell volume and the powder X-ray diffraction pattern itself. As previously mentioned the volume data suggest both order-disorder and compositional unmixing as possibilities. Unfortunately, the powder X-ray diffraction pattern itself can only be used as a suggestion of the unmixing, because most likely is the possibility that three phases are present in the experimental results—the two unmixed phases plus the starting mixed phase. Due to vector addition, the X-ray peaks tend to average to an intermediate value which would be identical to the peaks of the unmixed phase, and peak splitting would only be observed on one or two peaks. For jadeite-diopside peaks, splitting due to compositional unmixing could probably only be observed for the (220) reflection. This splitting is identical to the phenomenon reported from the solvus region in the enstatite-diopside system (Davis and Boyd, 1965).

For the case of order-disorder unmixing there is a space group difference: C2/c for the disordered; P_2 for the ordered. A few additional but extremely weak X-ray reflections occur for the ordered phase, and one of these is located near the (220) peak. It is not certain that this peak could be observed, but even if it could for certain orientations, it would be of low intensity. In any case it may not be possible to distinguish between order-disorder and compositional unmixing on the basis of the powder pattern alone. The relative intensities of split peaks while important in theory are not too meaningful in practice because of orientation problems. It is tempting to ignore one or two split peaks and index the X-ray pattern on the remaining reflections. This practice is misleading because as previously stated some of the single reflections are simply composites. The problem of trying to prove and analyze compositional unmixing is not unique with jadeite-diopside but exists to some degree in all other pyroxene systems that have been studied experimentally. A survey of investigators by personal communication has revealed identical problems of interpreting order-disorder and compositional unmixing in the following systems: the orthorhombic-monoclinic phases in enstatite-diopside (F. R. Boyd); the monoclinic phases in augite-hypersthene (A. Turnock); the monoclinic phases in enstatite-diopside (I. Kushiro). In each case (with the exception of some experiments with hedenbergite-ferrosilite where large crystals were grown hydrothermally) examination of the powder pattern showed exactly the same phenomena as that described above, namely peak splitting of usually only one peak and at most two peaks and composite averaging of these and other peaks.

In the present experiments with jadeite-diopside splitting of the (220) reflection was observed (table 1). It has been possible to demonstrate only the splitting in phases quenched from the 50:50 composition. The relative intensities are in a ratio of approximately 10:1 for the (220) to the additional peak. The actual limits and precise characterization of the

two-phase region, whether of compositional (1st order) or order-disorder (1st or 2nd order) type, is not known because of the sluggish nature of the system and contamination problems with the furnace cell and thermocouple for long-term experiments in this high-temperature range. Particularly on the basis of the volume measurements and, in addition, on the basis of the observance of the (220) split it seems that the temperature maximum will occur near to 1:1 molar composition. The splitting occurs at 1400°C but not at 1450°C when the pressure is 30 kb. Taking the critical temperature as approximately 1435°C and using the equations for critical unmixing (Guggenheim, 1949, p. 210 and following), one can calculate the pressure effect on the critical temperature. Assuming the entropy term (Sm) to be of the form

$$-R[(x_1 \ln x_1 + (1 - x_1) \ln (1 - x_1)],$$

the excess free energy of mixing ($\bar{G}m^e$) is of the form

$$(x_1)(1 - x_1)\, w$$

The w used here is sometimes called "Guggenheim's w" or the mismatch free energy. The quantity w has the dimensions of molar energy and is identical to Hildebrand's (1964) "interchange energy," which is the work done on the system by mixing. Guggenheim has shown that

$$w = 2RT$$

when T is critical. For 30 kb, 1708°K we have

$$w = 6.79 \text{ kcal/mole}$$
$$\text{and } x_{1(Tc)} = 0.5$$

Because the data do not violate Guggenheim's simple-mixture approximation, dw/dp can be calculated as a further consequence.

$$\bar{V}^e = (x_1)(1 - x_1)(dw/dp) = (x_1)(1 - x_1)\, 2.56$$

Accordingly,

$$\Delta w_{(30K)} = \frac{2.56}{41.83} \int_{30 \times 10^3}^{p} dp$$

Here the excess molar volume of mixing function has been written as an approximation to the measured data (table 2) and is compared in figure 5. Working back from this function it is possible to evaluate w at 50 kb in order to average the pressure effect:

$$w_{(50 \text{ kb})} = 6790 + \frac{(2.56)(20 \times 10^3)}{41.83}$$
$$= 8.015 \text{ kal/mole}$$

The Tc (50 kb) = w/2R = 2015°K = 1742°C. This can be written dw/dp = 15°/kb (for w independent of T). While there is no particular reason for the slope to be constant there is nonetheless a strong pressure

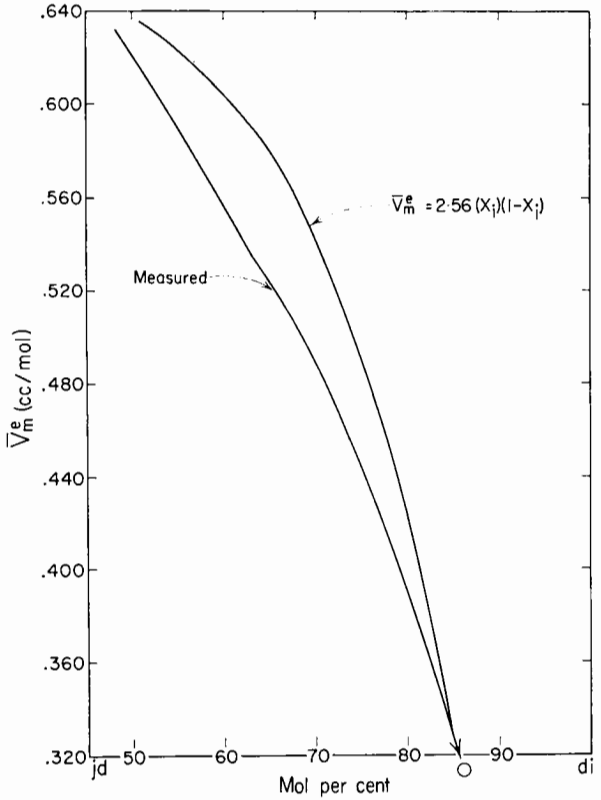


Fig. 5. Function for excess volume of mixing of jadeite-diopside solid solutions.

effect on the critical temperature so the two-phase region will occur at much lower temperatures at low pressures.

An attempt was made to unmix or disorder a natural omphacite for comparison with results in the synthetic system. The natural omphacite is an ordered, approximately 1/1 molar, jadeite-diopside from Kaminaljuj, Guatemala. This very pure omphacite was kindly supplied by Dr. J. Papike, who analyzed the experimental results by X-ray. The material was treated at 1350°C, 30 kb, for 6 hours. This was not enough time for complete equilibration, but it is significant that a very minor peak in addition to the (220) was observed. The pyroxene was determined to be completely ordered before the experiment (that is, $V^e = O$) on the basis of single crystal measurements. A positive value of excess volume was recorded after the experiment, however, only about one-half that reported for the synthetic product. This observation does tend to support the synthetic results.

Continuing with Guggenheim's simple-mixture approximation it is advantageous in lieu of experimental data to predict relations in the subsolidus. In particular, the reaction

$$(x)\ \underset{\text{Albite}}{NaAlSi_3O_8} + (x)\ \underset{\text{Nepheline}}{NaAlSiO_4} + (1-2x)\ \underset{\text{Diopside}}{CaMgSi_2O_6}$$
$$\rightleftharpoons$$
$$\underbrace{2xNaAlSi_2O_6 + (1-2x)\ CaMgSi_2O_6}_{\text{Omphacite}}$$

represents the breakdown of omphacite in silica-undersaturated rocks. In effect, diopside is added to the jadeite $\rightleftharpoons$ nepheline + albite univariant equilibrium. The purpose is to observe displacement of the boundary by taking into account the regular solution mixing terms. Using an omphacite of $Jd_{20}Di_{80}$ to calculate the effect of a strong dilution, it is helpful to look at the equilibrium pressure at room temperature. We therefore calculate the univariant shift by means of

$$P\Delta V = \Delta H^\circ - T\Delta S^\circ + RT\sum_{ij} x_i \ln x_j$$

for the reaction

$$Ab + Ne + (n)\ Di \rightleftharpoons Omphacite\ (nDi + 2Jd)$$

The analysis for this particular omphacite ($Jd_{20}Di_{80}$) is as follows

$$Ab + Ne + 8Pyx_{(Di)} \rightleftharpoons Pyx_{(Jd_{20}Di_{80})}$$

$$\Delta G_{298} = \Delta H^\circ - T\Delta S^\circ + RT(x_{Di} \ln x_{Di} + x_{Jd} \ln x_{Jd})$$
$$= -6700 + 298\ (14.7) + 1.99(298)\ (0.8 \ln 0.8 + 0.2 \ln 0.2)$$
$$\approx \Delta V(P) = 33.8\ P/41.83\ \text{cal/mole}$$
$$P_{\substack{\text{equil.}\\ 298^\circ}} = -3.3\ \text{kb (intercept)}$$
$$dT/dP = \frac{\Delta V + 0.01\ \Delta V}{\Delta S + 0.8 \ln 0.8 + 0.2 \ln 0.2} = 48^\circ\text{C/kb}$$

Except for the addition of the regular solution entropy of mixing term, this is the same expression used by Yoder and Weir (1951). Figure 6 compares the boundary for this omphacite breakdown with that of pure jadeite. The difference is slight indeed, amounting to an increase of 1.5 to 2 kb with nearly the same slope. Kushiro (1965) attempted to observe this effect with the analogous reaction Omp + Ab $\rightleftharpoons$ Omp + Qtz. He used glass as a starting material because only the two omphacites at equilibrium would be of the correct composition. Unfortunately, glass is a difficult starting material to work with because of metastable nucleation and, in particular, because of the great sensitivity on melting due to the presence of a small amount of water. It will be important to carry out these experiments with crystalline starting materials and to demonstrate reversibility by making the runs of sufficient duration for phase and compositional equilibrium. Kushiro's results at least are in accord with the theoretical predictions because they include a shift of 1 to 2 kb which is the same order of magnitude as that calculated.

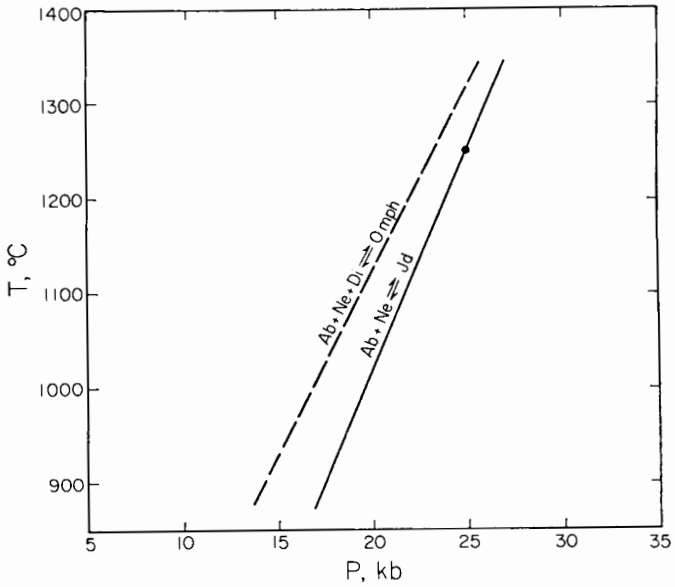


Fig. 6. Curves for Ab + Ne ⇄ Jd (after Bell and Rosebloom, 1965) and Ab + Ne + 8 Di + Omp (calculated).

That diopside will not seriously affect jadeite stability seems to have been borne out by a few recent experiments of Newton and Smith (1967). Using natural omphacites, they found that the results of Kushiro are not significantly changed, even if up to 10 wt percent acmite is present.

DISCUSSION

In studying the high-pressure melting relations in the system jadeite-diopside the purpose was to investigate some of the compositions so carefully examined by Bowen (1913), Schairer (1950), and by Schairer and Yoder (1960) at 1 atm. Clearly jadeite–diopside at high pressure is analogous to albite-anorthite at atmospheric pressure. Jadeite and diopside form extensive solid solutions in nature, and it was anticipated that the melting of these solid solutions would strongly concentrate Na_2O in magmatic liquids relative to pyroxenes in equilibrium with them but was found to be negligible. Perhaps the most significant information gained from the present study is that despite rather important changes in phase chemistry the melting process in the jadeite-diopside system follows Bowen's trend: The residual liquid is enriched in sodium and aluminum, and petrogeny's residua system is preserved.

The experimental results confirm in a general way that jadeite-diopside is a high-pressure analog of the albite-anorthite melting behavior. However, the solidus and liquidus are quite close together in temperature, and even though the fractionation process operates, there will be limited concentrations of jadeite constitutents in high-pressure magmas relative to their parent rocks. The situation may be complicated

if either a compositional two-phase or order-disorder region occurs. Calculations based on the two-phase maximum stability suggest that mixing diopside with jadeite will not have a strong effect on the breakdown reaction to albite and nepheline. The melting range found in this study is consistent with that of the phases that compose anhydrous peridotite in the Earth's mantle (Davis and Boyd, 1965).

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