[American Journal of Science, Vol. 249, September, 1951, Pp. 683-694]

CHANGE OF FREE ENERGY WITH PRESSURE OF THE REACTION NEPHELINE + ALBITE = 2 JADEITE

H. S. YODER AND C. E. WEIR

ABSTRACT. The change of free energy with pressure for the reaction nepheline + albite = 2 jadeite was computed from values of the density and compressibility determined by the writers and the unpublished thermal expansion data of Rosenholtz and Smith and was found to be very small.

INTRODUCTION

DIRECT experimental determination of the stability relations of jadeite has not been successful (Yoder, 1950), and for this reason the indirect thermodynamic approach has been adopted. By determining the thermodynamic properties of the phases in the assumed reaction:

$$\underset{\text{(albite)}}{NaAlSi_3O_8} + \underset{\text{(nepheline)}}{NaAlSiO_4} = 2\ \underset{\text{(jadeite)}}{NaAl(SiO_3)_2}$$

the pressure and temperature conditions under which this reaction may go can be computed. The following provisional thermodynamic values at a pressure of 1 atmosphere have been determined for the assumed reaction:

$\Delta S^\circ_{298.16} = -14.7$ cal/mol — Kelley (personal communication, 1949),

$\Delta H^\circ_{298.16} = -6700$ cal/mol — Kracek and Neuvonen (personal communication, 1950),

where S is the entropy and H the enthalpy. Since the change in free energy $\Delta F = \Delta H - T\Delta S$, the value of $\Delta F^\circ_{298.16}$ for the reaction is negative, and therefore jadeite is the more stable phase at room temperature and atmospheric pressure. When the high-temperature specific heats are known it will be possible to calculate the change in free energy, ΔF, for the assumed reaction at all temperatures at a pressure of 1 atmosphere.[1] Values of the free energy change for the assumed reaction at higher pressures can be calculated from the corresponding values at atmospheric pressure by the relation

$$\frac{\partial (\Delta F)}{\partial P} = \Delta V,$$

[1] The high-temperature specific heats of albite have been measured (White, 1919); it is anticipated that F. C. Kracek will determine the high-temperature specific heats of nepheline and jadeite at a later date.

where P is the pressure and V the volume. Using the densities, thermal expansions, and compressibilities of each phase, ΔV can be evaluated for the reaction as a function of both temperature and pressure. It is the purpose of this paper to report ΔV and $\frac{\partial (\Delta F)}{\partial P}$ for the assumed reaction, using the values of density and compressibility determined by the writers and the unpublished linear thermal expansion data of Rosenholtz and Smith (personal communication, 1950).

THERMAL EXPANSION

The linear thermal expansion data, kindly supplied by J. L. Rosenholtz and D. T. Smith of Rensselaer Polytechnic Institute, are given in table 1. The volume thermal expansion for albite (triclinic) was taken as the sum of the linear thermal expansions in the three axial directions; for jadeite (monoclinic), the sum of the linear thermal expansions in three orthogonal directions in a polycomponent specimen; for nepheline (hexagonal ?), the sum of the linear thermal expansions

TABLE 1

Thermal Expansion Data of Rosenholtz and Smith (unpublished)

Phase (Source)	$\alpha \times 10^6$ orientation	Interval of Temperature—from 20°C to 100	200	300	400	500	600	700	800
Albite (Amelia County, Va.)	‖a	11.52	12.03	12.68	13.24	13.61	14.12	14.32	14.68
	‖b	4.68	5.02	5.57	6.04	6.36	6.80	7.35	7.72
	‖c	0.71	1.47	2.65	3.63	4.43	5.16	5.88	6.68
	α_v (obs)	16.91	18.52	20.90	22.91	24.40	26.08	27.55	29.08
	α_v (calc)	16.76	18.85	20.83	22.70	24.45	26.09	27.62	29.04
Nepheline (Gooderham Ont., Canada)	‖c	9.11	10.96	11.83	13.09	14.48	15.67	16.02	15.91
	⊥c	13.37	15.44	16.92	17.97	19.34	20.29	20.95	21.47
	α_v (obs)	35.85	41.84	45.67	49.03	53.16	56.25	57.92	58.85
	α_v (calc)	36.03	41.26	45.94	49.78	53.08	55.73	57.74	59.10
Jadeite (Burma, USNM 94829)	A	7.75	8.24	8.62	8.97	9.06	9.53	10.01	——
	B	6.55	7.13	7.57	7.92	8.25	8.74	9.26	——
	C	6.37	6.89	7.29	7.58	7.85	8.34	8.82	——
	α_v (obs)*	20.67	22.26	23.48	24.47	25.16	26.61	28.09	——
	α_v (calc)	20.89	22.06	23.23	24.39	25.56	26.72	27.89	——

*A distinct small change beginning at 510° and ending at 525° was exhibited by all specimens. The coefficient of volume thermal expansion in this temperature range has a value of 41.19 x 10^{-6}; this change was neglected in the calculations. Only values up to 700° need be considered since jadeite melts metastably at a temperature at least as low as 800° after long heating.

parallel to c plus twice that perpendicular to the c axis.[2] The volume thermal expansions, α_v, are expressed in terms of the following equations obtained by the method of least squares:

$$\alpha_{Ab} = 15.00 \times 10^{-6} + 2.240 \times 10^{-8}(t\text{-}20) - 5.65 \times 10^{-12}(t\text{-}20)^2$$
$$\alpha_{Ne} = 31.39 \times 10^{-6} + 6.063 \times 10^{-8}(t\text{-}20) - 32.17 \times 10^{-12}(t\text{-}20)^2$$
$$\alpha_{Jd} = 19.96 \times 10^{-6} + 1.166 \times 10^{-8}(t\text{-}20),$$

where t is temperature in °C and α_{Ab} is the coefficient of volume thermal expansion of albite. The numerical constants in the above equations, as well as those following, are carried out to the number of figures indicated only for internal consistency.

Since $V = V_o(1 + \alpha t)$ the volume at any temperature at 1 atmosphere can be obtained. The molal volumes of the phases can be computed from the measured densities of the specimens used and their theoretical molecular weights:

Phase	Density 20° C	Mol Wt.	Molal Vol.
Albite (Amelia, Va.)	2.605	262.15	100.633
Nepheline (Gooderham, Ont.)	2.616	142.03	54.293
Jadeite (Burma)	3.328	202.09	60.724

The molal volume of each phase at temperatures between 293° and 973° K and at a pressure of 1 atmosphere can be found by the equations:

$$V_{Ab} = 100.399 + 0.42 \times 10^{-4}T + 2.754 \times 10^{-6}T^2 - 5.68 \times 10^{-10}T^3$$
$$V_{Ne} = 54.120 - 6.75 \times 10^{-4}T + 4.827 \times 10^{-6}T^2 - 17.47 \times 10^{-10}T^3$$
$$V_{Jd} = 60.430 + 7.97 \times 10^{-4}T + 0.708 \times 10^{-6}T^2,$$

where T is the temperature in °K and V is the molal volume in cc/mol.

COMPRESSIBILITY

The apparatus and experimental method for obtaining the compressibilities of the phases have been described previously (Weir, 1950). The equipment and methods were designed to conform closely to those used successfully by workers at the Geophysical Laboratory. The present apparatus differs only in slight modifications of the pressure vessel and accessories and in that the shunted-decade type Wheatstone bridge was used to measure the resistance of the manganin pressure gage.

An experiment consists of determining the pressure and the corresponding displacement of a leak-proof piston (Bridg-

[2] The volume thermal expansions obtained in the manners described for albite and jadeite are approximations; for discussion see Wooster (1938, 25-27).

man, 1914) which is forced into a pressure vessel containing the specimen immersed in varsol. A similar experiment performed with a steel bar of nearly equivalent volume permits the calculation of the compressibility of an unknown material in terms of the steel bar whose compressibility is known (Bridgman, 1940, 1949). Equations for this calculation have been outlined by Adams, Williamson, and Johnston (1919).

The materials investigated are described below.

Albite. Varuträsk, Sweden. Collected by Th. G. Sahama. Contains less than 3 per cent impurities. Density at 25.6° C = 2.641. An analysis of the purified material by E. G. Zies shows:

SiO_2	68.76	MgO	0.00
Al_2O_3	19.50	Na_2O	11.51
Fe_2O_3	0.13	K_2O	0.13
TiO_2	0.00	P_2O_5	0.02
CaO	0.13	H_2O	0.08
		Total	100.26

The thermal expansion data on this material were considered unsatisfactory by Rosenholtz because of the presence of a significant amount of quartz and because of residual strains within the deformed material. Unfortunately the albite from Amelia County, Virginia, was not suitable for the compressibility experiments.

Oligoclase. Same cylinder used by Adams and Williamson (1923). No chemical analysis was made; the optical properties indicate An_{22}. On the basis of X-ray evidence, O. F. Tuttle gives An_{23}.

Burmese Jadeite. Same cylinder used by Adams and Gibson (1929). USNM 94829. On microscopic examination, H. E. Merwin found the material to be practically pure jadeite. An analysis by E. G. Zies has been published recently (Yoder, 1950, p. 229). The material used for the thermal expansion work was cut from the same hand specimen.

Japanese Jadeite. Cylinders were cut from a specimen from Kotaki, Japan. USNM 105860. Microscopic examination revealed considerable analcite. An analysis by O. von Knorring will soon be published by F. C. Kracek and K. J. Neuvonen. Analyses of similar material are given by Kawano (1939). Density at 24.2° C = 3.189.

Nepheline. Collected by J. F. Schairer 1.5 miles southeast of Gooderham, Ontario, Canada. Cut from the same crystal used in the thermal expansion experiments. Microscopic examination indicated the material to be virtually free of impurities. An analysis of selected material by E. G. Zies shows:

SiO_2	43.60	Na_2O	15.82
Al_2O_3	34.02	Li_2O	0.01[2]
Fe_2O_3	0.10	K_2O	5.47
TiO_2	trace[1]	MnO	trace[1]
CaO	0.75	Ign (850° C)	0.16
MgO	0.04		
		Total	99.97

[1]Present but in amounts less than 0.01 per cent.

[2]Lithium is definitely present and the amount is about 0.01 per cent.

The high potash content may affect the compressibility and expansivity. However, from what is known about the relative behavior of soda and potash compounds (for example, albite and orthoclase), the potash-bearing nepheline used in the measurements probably gives results close to those to be expected from pure soda nepheline. The small amount of lime and the excess silica probably do not influence measurably the result.

The results of the individual measurements of decrease in volume are given in table 2 and the average values are shown graphically in figure 1. The relation of the values for the feldspars to other members of the plagioclase series is presented in figure 2.

Data obtained under two slightly different experimental conditions are recorded separately in table 2. Determinations were made with the micrometer dial gage, used to measure piston displacement, mounted on the upper (movable) platen of the hydraulic press. This method of mounting appeared to introduce noticeable irregularities in the measurements of the highly incompressible jadeite. More reproducible results for these materials were obtained with the dial gage mounted directly on the ram actuating the leak-proof piston. Data obtained with the latter arrangement were assigned double weight in calculating the average $-\frac{\Delta V}{V_o}$.

TABLE 2

Results of Compressibility Measurements

Burmese Jadeite

$V_o = 20.097$cc $a = 0.198 \times 10^{-3}$ $b = 0.747 \times 10^{-6}$ $c = 0.21 \times 10^{-11}$

P atm	$-\frac{\Delta V}{V_o}$, Exptl[1]	$-\frac{\Delta V}{V_o}$, Exptl[1]	$-\frac{\Delta V}{V_o}$, Av Exptl	$-\frac{\Delta V}{V_o}$, Calc
10,000	0.00620	0.00633	0.00627	0.00630
9000	552	567	560	553
8000	457	471	464	476
7000	398	408	403	398
6000	319	333	326	322
5000	250	249	250	246
4000	171	169	170	170
3000	91	89	90	95
2000	00	00	00	–0.00020
1000	–0.00087	–0.00102	–0.00095	

Japanese Jadeite

$V_o = 20.167$cc $a = 0.382 \times 10^{-3}$ $b = 1.11 \times 10^{-6}$ $c = -1.5 \times 10^{-11}$

P atm	$-\frac{\Delta V}{V_o}$, Exptl[1]	$-\frac{\Delta V}{V_o}$, Exptl[1]	$-\frac{\Delta V}{V_o}$, Av Exptl	$-\frac{\Delta V}{V_o}$, Calc
10,000	0.00855	0.00814	0.00835	0.00828
9000	755	720	738	744
8000	668	643	656	652
7000	558	546	552	556
6000	455	465	460	459
5000	362	361	362	358
4000	258	258	258	255
3000	142	148	145	147
2000	000	000	000	–0.00038
1000	—	–0.00112	–0.00112	

Swedish Albite

$V_o = 20.122$cc $a = 0.04 \times 10^{-3}$ $b = 2.02 \times 10^{-6}$ $c = -2.16 \times 10^{-1}$

P atm	$-\frac{\Delta V}{V_o}$, Exptl[1]	$-\frac{\Delta V}{V_o}$, Exptl[1]	$-\frac{\Delta V}{V_o}$, Av Exptl	$-\frac{\Delta V}{V_o}$, Cal
10,000	0.01504	0.01472	0.01488	0.0148
9000	1327	1301	1314	131
8000	1161	1131	1146	113
7000	978	952	965	96
6000	801	765	783	77
5000	599	581	590	59
4000	406	391	398	39
3000	209	208	208	2(
2000	000	000	000	–0.000

Nepheline

$V_o = 19.812$cc $a = 0.26 \times 10^{-3}$ $b = 2.05 \times 10^{-6}$ $c = -0.52 \times 10^{-11}$

P atm	$-\frac{\Delta V}{V_o}$, Exptl[1]	$-\frac{\Delta V}{V_o}$, Exptl[2]	$-\frac{\Delta V}{V_o}$, Exptl[2]	$-\frac{\Delta V}{V_o}$, Av Exptl	$-\frac{\Delta V}{V_o}$, Calc
10,000	0.01640	0.01640	0.01613	0.01638	0.01633
9000	1452	1432	1420	1439	1436
8000	1254	1214	1232	1238	1237
7000	1041	1033	1005	1030	1038
6000	844	844	861	848	838
5000	640	629	667	644	636
4000	430	417	456	433	434
3000	223	222	253	230	230
2000	000	000	000	000	-0.00026
1000	-0.00232	—	—	-0.00232	

Oligoclase

$V_o = 20.124$cc $a = 0.004 \times 10^{-3}$ $b = 1.79 \times 10^{-6}$ $c = -1.34 \times 10^{-11}$

P atm	$-\frac{\Delta V}{V_o}$, Exptl[1]	$-\frac{\Delta V}{V_o}$, Exptl[2]	$-\frac{\Delta V}{V_o}$, Exptl[2]	$-\frac{\Delta V}{V_o}$, Av Exptl	$-\frac{\Delta V}{V_o}$, Calc
10,000	0.01342	0.01296	0.01396	0.01344	0.01344
9000	1210	1147	1227	1199	1186
8000	998	1007	1038	1010	1024
7000	861	856	883	865	861
6000	697	678	729	701	695
5000	535	519	508	524	525
4000	361	349	329	350	353
3000	184	179	165	178	178
2000	000	000	000	000	000
1000	-0.00186	—	—	-0.00186	

[1] Observations with dial gage mounted directly on ram.
[2] Observations with dial gage mounted on platen of press.

Three measurements of relative volume change are reported for oligoclase and nepheline while two measurements are reported for each of the jadeite specimens and the Swedish albite. The relative volume change, $-\frac{\Delta V}{V_o}$, is equal to $\frac{V_{2000} - V_P}{V_o}$ where V_0 is the volume at atmospheric pressure, V_P is the volume at the pressure P, and V_{2000} is the volume at 2000 atmospheres. Average values of the volume change were obtained by weighting the values as described above. The average experimental values shown in table 2 are well represented by the equation:

$$-\frac{\Delta V}{V_o} = a + b(P\text{-}2000) + c(P\text{-}2000)^2.$$

This equation was fitted to the data by the method of least squares and the values of the constants a, b, and c so obtained are recorded in table 2. Values of the decrease in volume calculated by means of the equation are recorded for each pressure and may be compared with the average experimental values. The data for Burmese jadeite and oligoclase agree well with the experimental data previously reported (Adams and Gibson, 1929; Adams and Williamson, 1923) on the same specimens if it is noted that the earlier values are in terms of megabaryes, which at the time those papers were written was the name given to the pressure unit now called the bar.

The value of the compressibility β, equal to $-\frac{1}{V_0}\frac{dV}{dP}$, may be obtained by differentiating the above equation:

$$\beta = b - 4000c + 2cP.$$

In order to obtain the value of the specific molal volume change, the compressibility expression is integrated between the limits of $P_0 = 0$ and $P_1 = P$:

$$\Delta V = -V_0 [(b-4000c)P + cP^2].$$

This procedure involves the assumption that the expression

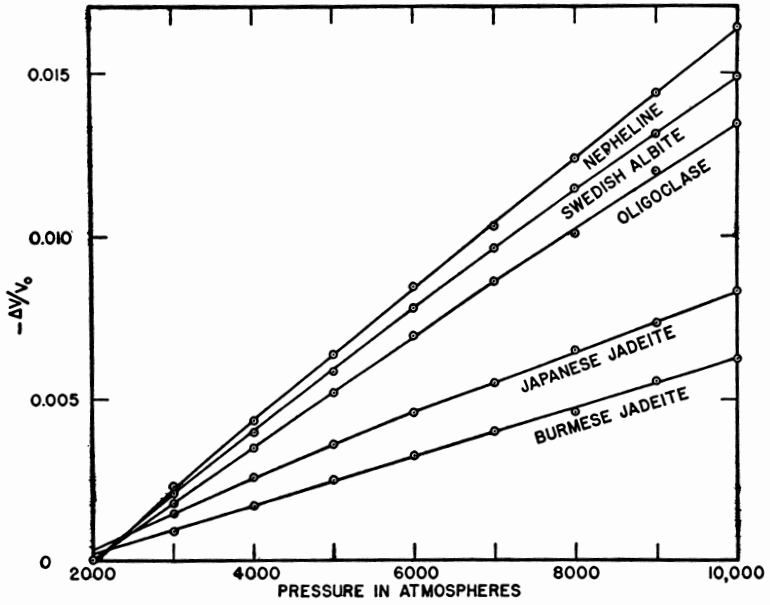

Figure 1. Relative volume change as a function of pressure for selected natural minerals.

for β, which was experimentally determined between the limits of 2000 and 10,000 atmospheres, is valid in the region of 0 to 2000 atmospheres.

Assuming that the temperature coefficient of the compressibility is negligible, the change in molal volume of the phases in the assumed reaction at $T = 298^\circ$ K and for pressures between 0 and 10,000 atmospheres is given by the following equations:

$$\Delta V_{Ab} = -2.123 \times 10^{-4}P + 2.17 \times 10^{-9}P^2 \text{ cc/mol}$$
$$\Delta V_{Ne} = -1.113 \times 10^{-4}P + 0.28 \times 10^{-9}P^2 \text{ cc/mol}$$
$$\Delta V_{Jd} = -0.449 \times 10^{-4}P - 0.13 \times 10^{-9}P^2 \text{ cc/mol}$$

where the subscript Ab refers to the data for the Swedish albite; Ne, nepheline; and Jd, Burmese jadeite.

It is to be noted that the sign of the coefficient of the P^2 term for ΔV_{Jd} is negative. It is, however, unlikely that the rate at which the volume decreases would increase with pressure. The negative value is merely indicative of the experimental error and indicates that for materials of low compressibility the piston displacement method is not capable of detecting small changes in the compressibility.

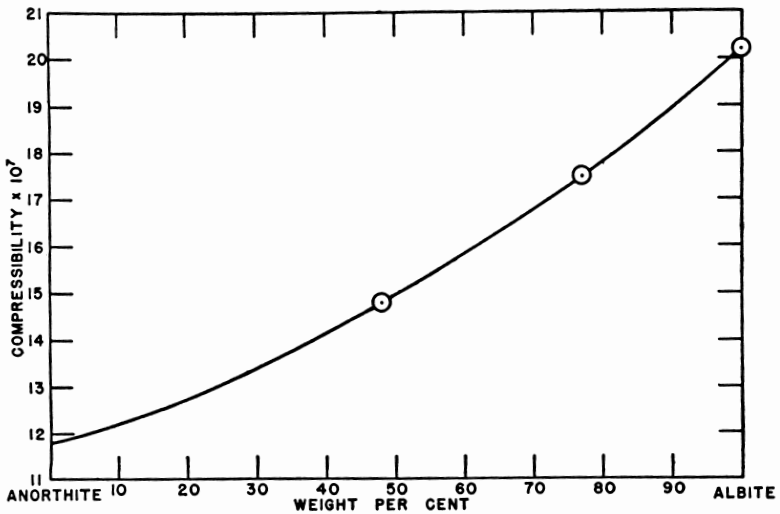

Fig. 2. Compressibility of plagioclase feldspars. Points are based on an average of new data and the data of Adams and Gibson (1929) and Adams and Williamson (1923).

RESULTS OF COMPUTATIONS

By combining the results of the thermal expansion and compressibility experiments, the molal volumes of each phase as a function of pressure, P, in atmospheres and temperature, T, in °K are:

$$V_{Ab} = 100.399 + 0.42 \times 10^{-4}T + 2.754 \times 10^{-6}T^2 - 5.68 \times 10^{-10}T^3 - 2.123 \times 10^{-4}P + 2.17 \times 10^{-9}P^2 \text{ cc/mol}$$

$$V_{Ne} = 54.120 - 6.75 \times 10^{-4}T + 4.827 \times 10^{-6}T^2 - 17.47 \times 10^{-10}T^3 - 1.11 \times 10^{-4}P + 0.28 \times 10^{-9}P^2 \text{ cc/mol}$$

$$V_{Jd} = 60.430 + 7.97 \times 10^{-4}T + 0.708 \times 10^{-6}T^2 - 0.449 \times 10^{-4}P - 0.13 \times 10^{-9}P^2 \text{ cc/mol.}$$

The change in volume for the assumed reaction is given by $\Delta V = 2V_{Jd} - (V_{Ab} + V_{Ne})$. The expression of the volume change of the assumed reaction is:

$$\Delta V = -33.660 + 22.27 \times 10^{-4}T - 6.166 \times 10^{-6}T^2 + 23.15 \times 10^{-10}T^3 + 2.339 \times 10^{-4}P - 2.71 \times 10^{-9}P^2 \text{ cc/mol,}$$

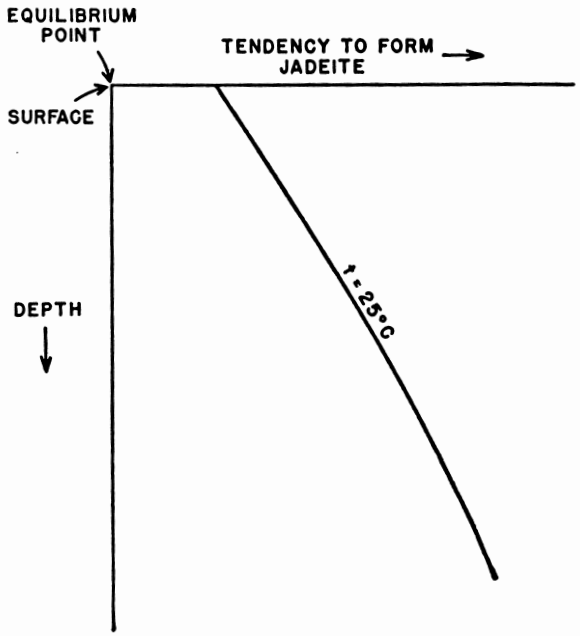

Fig. 3. Schematic diagram indicating the tendency to form jadeite ($-\Delta F$) from the reaction nepheline + albite → 2 jadeite as a function of depth in the earth (P).

and the change of free energy with pressure is:

$$\frac{\partial(\Delta F)}{\partial P} = -0.8148 + 0.539 \times 10^{-4}T - 0.1492 \times 10^{-6}T^2 + 0.560 \times 10^{-10}T^3 + 0.0566 \times 10^{-4}P - 0.066 \times 10^{-9}P^2,$$

with ΔF in calories per mol, P in atmospheres, and T in °K.

In order to illustrate the magnitude of the volume term and the change of free energy with pressure, the numerical calculations have been made for the extremes of temperature and pressure:

P atm.	T °K	ΔV cc/mol	$\frac{\partial(\Delta F)}{\partial P}$
1	293	−33.478	−0.8104
1	973	−35.261	−0.8520
10,000	293	−31.411	−0.7603
10,000	973	−33.193	−0.8020

The effect of pressure on the change of free energy is evidently very small for the assumed reaction.

GEOLOGICAL IMPLICATION

From the thermodynamic values obtained by Kelley and by Kracek and Neuvonen, it can be stated with certainty that jadeite does not require pressure for its formation at room temperature. The present calculations show that pressure *favors* the formation of jadeite, but at a slowly decreasing rate. Stated in another way, the tendency to form jadeite increases at a decreasing rate at greater depths in the earth; this is shown schematically in figure 3. No estimate of the free energy of activation required, that is, the energy barrier which must be overcome before the reaction will actually proceed, can be made at this time.

ACKNOWLEDGMENT

The writers wish to acknowledge the role played by Dr. L. H. Adams, Director of the Geophysical Laboratory, through whose persuasion over a period of years much of the data on the minerals described were obtained by the various investigators.

References

Adams, L. H., and Gibson, R. E., 1929. The elastic properties of certain basic rocks and of their constituent minerals: Nat. Acad. Sci. Proc., vol. 15, pp. 713-724.

———, and Williamson, E. D., 1923. The compressibility of minerals and rocks at high pressures: Franklin Inst. Jour., vol. 195, pp. 475-529.

———, ———, and Johnston, J., 1919. The determination of the compressibility of solids at high pressures: Am. Chem. Soc. Jour., vol. 41, pp. 12-42.

Bridgman, P. W., 1914. The technique of high pressure experimenting: Am. Acad. Sci. Proc., vol. 49. pp. 627-643.

———, 1940. The linear compression of iron to 30,000 kg/cm^2: Am. Acad. Arts Sci. Proc., vol. 74, pp. 11-20.

———, 1949. Linear compressions to 30,000 kg/cm^2, including relatively incompressible substances: Am. Acad. Arts Sci. Proc., vol. 77, pp. 187-234.

Kawano, Y., 1939. A new occurrence of jade (jadeite) in Japan and its chemical properties: Jour. Japanese Assoc. Mineralogists, Petrologists and Economic Geologists, vol. 22, pp. 195-201. (In Japanese)

Weir, C. E., 1950. High pressure apparatus for compressibility studies and its application to measurements on leather and collagen: Nat. Bur. Standards Jour. Research Standards, vol. 45, pp. 470-477, Research Paper 2160.

White, W. P., 1919. Silicate specific heats; Second Series: Am. Jour. Sci., 4th Ser., vol. 47, pp. 1-43.

Wooster, W. A., 1938. A text-book on crystal physics, The University Press, Cambridge, England.

Yoder, H. S., 1950. The jadeite problem: Am. Jour. Sci., vol. 248, pp. 225-248, 312-334.

Geophysical Laboratory
Carnegie Institution of Washington
Washington, D. C.

National Bureau of Standards
Washington, D. C.