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Phase Relationships of I-Type Granite With H₂O to 35 Kilobars: The Dinkey Lakes Biotite-Granite From the Sierra Nevada Batholith

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The Dinkey Lakes biotite-granite from the Sierra Nevada batholith was reacted (with varying percentages of H_2O in sealed platinum capsules) in a piston-cylinder apparatus between 10 and 35 kbar. The results were combined with the results from previously published experiments to provide comprehensive phase relationships for an I-type granite: a P-T diagram with excess H_2O; isobaric $T-X_{H_2O}$ diagrams at 25, 30, and 35 kbar showing H_2O-undersaturated relations; the H_2O-undersaturated liquidus surface mapped with contours for constant H_2O contents and fields for near-liquidus minerals; and the solubility of H_2O in granite liquids to 35 kbar. Results and their implications show: (1) The solidus temperature decreases from 680°C at 2 kbar to 620°C at 10 kbar, then increases to 700°C at 35 kbar because of changes from less dense to more dense subsolidus mineral assemblages. (2) The melting interval with excess H_2O, which is only 35°C at 2 kbar, increases to 105°C at 10 kbar and 150°C at 35 kbar because the liquidus minimum in the complex rock system departs from granite composition with increasing pressure. (3) The solubility of H_2O in granite liquid is 27 ± 2.5 weight percent at 35 kbar and 850°C, indicating that a miscibility gap persists between H_2O-saturated silicate magmas and aqueous vapor phase, at least to pressures corresponding to 120-km depth in the mantle. Dissolution of alkali feldspar (20% of rock) in the subsolidus aqueous vapor phase indicates that deep-seated aqueous fluids are concentrated solutions. (4) Quartz and coesite are the liquidus minerals at mantle pressures for all H_2O contents, indicating that granites and rhyolites cannot be primary magmas from mantle peridotite or subducted oceanic gabbroic crust. (5) The liquidus surface at crustal pressures, with plagioclase and quartz as primary minerals, indicates that primary liquids of granite composition with moderate H_2O contents can be generated in the crust at reasonable temperatures; these liquids could rise to near surface levels without vesiculation. Granite liquid together with residual crustal minerals could constitute plutonic magmas of intermediate composition.

INTRODUCTION

Chappell and White [1974] identified two distinctly different types of granitoid rocks in southeastern Australia that they designated I-type and S-type. *White and Chappell* [1977] discussed their derivation by partial melting of igneous or sedimentary source rocks, respectively. The granitoid rocks of the Sierra Nevada batholith, with abundant hornblende [*Bateman et al.,* 1963], correspond to the I-type.

The Dinkey Lakes biotite-granite is one of a series of four rocks from the central Sierra Nevada batholith (with a tonalite and two granodiorites) that were studied in the presence of excess H_2O by *Piwinskii* [1968a, 1973], initially to 3 kbar and then to 10 kbar. Additional results on the tonalite were presented by *Lambert and Wyllie* [1974]—excess H_2O relationships to 30 kbar and 850°C; *Stern and Wyllie* [1973b, 1978]—30 kbar results for H_2O contents from 0% to excess; *Stern et al.* [1975]—completed PT diagram with excess H_2O to 30 kbar and the H_2O-undersaturated liquidus surface. Additional results on the granite have been presented by *Boettcher and Wyllie* [1968a]—near-solidus results with excess H_2O from 10–30 kbar; *Stern and Wyllie* [1973a, b]—completed PT diagram with excess H_2O to 35 kbar, preliminary results for 25 kbar with variable H_2O content, and results at 30 kbar with 5% H_2O; *Stern et al.* [1975]— the H_2O-undersaturated liquidus surface.

In this paper we present the complete phase relationships for the Dinkey Lakes biotite-granite (consolidated from the

scattered publications) together with previously unpublished run data, as representative for an I-type granite. Similar data for a muscovite granite, with mineralogy corresponding to an S-type granite, are presented in a companion paper [*Huang and Wyllie,* 1981].

THE DINKEY LAKES BIOTITE-GRANITE

The porphyritic biotite granite from the Dinkey Lakes region of the Sierra Nevada was provided by P. C. Bateman and F. C. Dodge of the U. S. Geological Survey. The geology of the area and the mineralogy and petrology of the granitic rocks were summarized by *Bateman et al.,* [1963]. The rock is number HL-29 in the account by *Kistler et al.* [1965] and number 104 in the system of *Piwinskii* [1968a].

Table 1 provides a chemical analysis for the rock, its CIPW norm, and its mode as determined by F. C. Dodge using stained slabs. *Piwinskii* (1968b) listed the Niggli value and Differentiation Index. The rock consists of nearly equal proportions of quartz, alkali feldspar, and plagioclase, with less than 5 volume percent mafic minerals, dominantly biotite. The alkali feldspar has the composition $Or_{79}Ab_{21}$, and the plagioclase is zoned form $An_{16}Ab_{84}$ to An_8Ab_{92} [*Piwinskii,* 1968b].

EXPERIMENTAL PROCEDURES

With measured amounts of distilled and deionized water the powdered rock sample (passed through 200 mesh) was sealed within platinum capsules and reacted in a single-stage piston-cylinder apparatus [*Boyd and England,* 1960], using a half-inch diameter tungsten carbide pressure chamber with

TABLE 1. Chemistry and Mineralogy of Dinkey Creek Biotite-Granite #104

Chemical Analysis		CIPW Norm	
SiO₂	75.4	Qz	31.6
TiO₂	0.15	Or	27.2
Al₂O₃	13.5	Ab	34.1
Fe₂O₃	0.0	An	5.0
FeO	0.64	Hy	0.6
MnO	0.04	Il	0.3
MgO	0.10	Mode	
CaO	1.0		
Na₂O	4.0	Quartz	34.8
K₂O	4.6	K-feldspar	29.0
H₂O⁺	0.35	Plagioclase	31.5
H₂O⁻	0.04	Mafic minerals,	4.7
P₂O₅	0.07	mostly biotite	
CO₂	<0.05		
Total	99.94		

Sample provided by P. C. Bateman and F. C. Dodge.

hardened steel liner and talc sleeves and cylinders in the furnace assembly. Grease-base 'Molykote-G' (MoS₂) served as a lubricant between the pressure chamber and the furnace assembly, which was jacketed with lead foil. All runs were brought to final pressure by the hot piston-out procedure [*Boyd et al.*, 1967]: pressure was raised 5 to 7 kbar above run pressure, the sample was heated to the run temperature, and
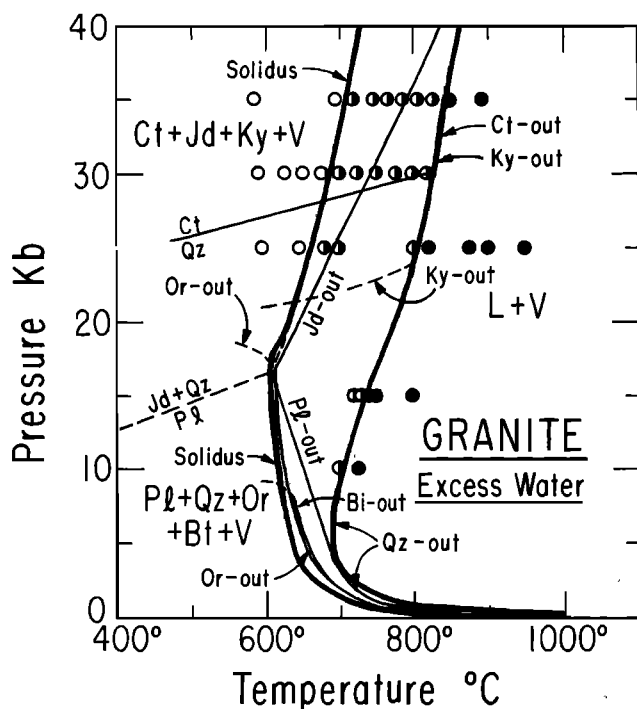

Fig. 1. Phase relations for biotite-granite (#104) with excess water. Definitive experiments are listed in Table 2. Phase boundaries below 3 kbar are from *Piwinskii* [1968a], and those between 3 and 25 kbar incorporate the results of *Piwinskii* [1973] and *Boettcher and Wyllie* [1968a]. Solid circles are runs above the liquidus, empty circles are subsolidus runs, and half-filled circles represent crystals + liquid. Dashed lines: phase boundaries estimated or uncertain. Abbreviations: Pl, plagioclase; Qz, quartz; Or, orthoclase; Bt, biotite; Jd, jadeite; Ct, coesite; Ky, kyanite; L, liquid; V, vapor. At low pressures, a single feldspar would replace Ab + Or at temperatures above the solvus.

the pressure was released to the run value. The nominal pressure without friction correction is considered accurate to ± 5% [*Huang and Wyllie*, 1975]. Thermocouples used were chromel-alumel ($T \leq 850°C$) and Pt/Pt 10 Rh ($T > 850°C$), with no correction for pressure effects on output emf. Temperatures are precise to ±5°C, and probably accurate to within ±13°C at 1000°C, 30-kbar pressure, considering pressure effects on thermocouple emf [*Getting and Kennedy*, 1971; *Merrill and Wyllie*, 1975]. The oxygen fugacity imposed on the reactants by the furnace assembly was slightly below the Ni/NiO buffer [*Merrill and Wyllie*, 1975].

Boettcher and Wyllie [1968a] found that above 15.3 kbar, metastable melting of this granite could occur below the solidus unless the high pressure mineral assemblage was used. Therefore, most runs above 15 kbar were performed in two stages. First, the sample was held below the metastable extension of the solidus curve long enough to produce the high-pressure mineral assemblage, and then the temperature was raised to the required level for the run. These two stages are indicated by pairs of rows in the run tables. Normal, single-stage runs were used at near-liquidus temperatures, above 950°C.

The reversibility of some phase boundaries was established by two-stage runs that were first held at temperature above the phase boundary, and then the temperature was lowered to the required level for the run. Details of problems and procedures for establishing reversibility of phase boundaries for rock samples within narrow temperature intervals were reviewed by *Stern and Wyllie* [1975].

Runs were quenched rapidly by switching off the power to the furnace. The capsules were recovered, tested for leaks by the application of gentle heat, and the sample was recovered and crushed for examination.

Identification of Phases

Phase assemblages were determined by optical and X ray studies of the quenched materials, as described by *Piwinskii* [1968a, 1973] and *Boettcher and Wyllie* [1968a]. Phases present at run conditions included crystals, silicate liquid containing dissolved H₂O, and a dense aqueous fluid phase containing dissolved solid components. Original crystals were preserved during the quench; liquids quenched to glasses; and the vapor phase quenched to water and a variety of precipitated solids.

Minerals encountered include quartz, coesite, plagioclase, jadeite, kyanite, garnet, and orthoclase-hydrate. Plagioclase and orthoclase-hydrate were positively identified only with X ray powder diffraction patterns. Euhedral prisms of quartz and coesite were easily identified. Jadeite occurred as small distinctive acicular prisms, while kyanite formed larger needles and clear euhedral prisms, often curved, with low birefringence and near-parallel extinction. Positive identification of kyanite was achieved with the electron microprobe. Small grains of garnet were easily identified optically.

All runs in the vapor-present region contained deposits from vapor such as quench mica and brown aggregates, which were described by *Boettcher and Wyllie* [1968a]. Glasses in the H₂O-saturated region were filled with cavities, as were some glasses in the vapor-absent region, indicating that exsolution of vapor from liquids occurred during the quench. Many runs in the vapor-absent region contained glasses with no cavities. The glasses from any one run usually appeared to be homogeneous.

TABLE 2. Definitive Experimental Runs for Granite #104 With Excess Water

Run	Pressure, kbar	Temperature, °C	Water Added, wt %	Time, hours	Phases Present
93	10	700	50	75	Qz, L, V
50	10	725	50	20	L, V
56	15	720	50	23	Qz, L, V
70	15	730	50	18	Qz, L, V
48	15	740	50	24	L, V
102	15	745	25	13	L, V
46	15	800	50	10	L, V
60R	15	900	50	6	Qz, L, V
		675	—	16	
44R	22.5	900	50	8	—
		750	—	15	Qz, Ky, L, V
53T	25	595	50	7	Qz, Ky, L, V
		750	—	16	
57T	25	595	50	7	—
		775	—	16	Qz, Ky, L, V
51T	25	595	50	6	—
		800	—	14	Ky, L, V
49T	25	595	50	6	—
		850	—	16	Ky, L, V
90T	25	595	50	6	—
		925	—	12	Ky, L, V
89T	25	595	50	6	—
		950	—	12	L, V
64	25	595	25	6	Qz, Jd, Ky, V
88T	25	595	25	6	—
		645	—	16	Qz, Jd, Ky, V
62T	25	595	25	8	—
		680	—	12	Qz, Jd, Ky, L, V
79T	25	595	25	6	—
		700	—	16	Qz, Ky, L, V
99T	25	595	25	6	—
		800	—	16	Qz, Ky, L, V
106T	25	595	25	6	—
		825	—	15	L, V
97T	25	595	25	6	—
		875	—	13	L, V
96T	25	595	25	6	—
		900	—	12	L, V
95T	25	595	25	5	—
		950	—	8	L, V
222T	30	590	33	6	—
		725	—	14	Ct, Jd, Ky, L, V
218	30	800	33	14	Ct, Ky, L, V
233	30	590	30	6	Ct, Jd, Ky, V
267T	30	590	30	6	—
		675	—	14	Ct, Jd, Ky, V
81T	30	590	26	6	—
		700	—	16	Ct, Jd, Ky, L, V
221T	30	590	26	6	—
		725	—	14	Ct, Jd, Ky, L, V
185T	30	590	26	6	—
		750	—	16	Ct, Ky, L, V
219T	30	590	26	6	—
		775	—	16	Ct, Ky, L, V
290T	30	590	25	6	—
		625	—	12	Ct, Jd, Ky, V
278T	30	590	25	6	—
		650	—	12	Ct, Jd, Ky, V
216	30	800	25	12	Ct, Ky, L, V
215	30	820	25	12	Ct, Ky, L, V
85T	35	585	50	6	—
		780	—	14	Ct, Ky, L, V
71T	35	585	50	6	—
		800	—	16	Ct, Ky, L, V
73T	35	585	50	6	—
		825	—	17	Ky, L, V
61T	35	585	50	10	—
		850	—	12	Ky, L, V
91T	35	585	50	6	—
		950	—	11	L, V
126T	35	585	30	6	—
		785	—	16	Ct, Jd, Ky, L, V

TABLE 2. (continued)

Run	Pressure, kbar	Temperature, °C	Water Added, wt %	Time, hours	Phases Present
123T	35	585	30	6	—
		805	—	16	Ct, Ky, L, V
118T	35	585	28	6	—
		825	—	16	Ct, Ky, L, V
119T	35	585	28	6	—
		850	—	16	L, V

All runs conducted in Pt capsules. Abbreviations: Qz, quartz; Ct, coesite; Jd, jadeite; Ky, kyanite; L, liquid; V, vapor. Runs occupying double rows were completed in two stages: T—after holding the sample at subsolidus conditions indicated in the first row, it was transferred to conditions indicated in the second row. R—after holding the sample above the liquidus at conditions indicated in the first row, it was transferred to conditions indicated in the second row.

EXPERIMENTAL RESULTS

Phase Relationships With Excess H_2O

Figure 1 shows the P-T projection for the melting interval of the granite with excess water; definitive runs from this study are listed in Table 2. The melting relations with excess water at 1, 2, 3, 5, and 10 kbar were determined by *Piwinskii* [1968*a*, 1973]. The near-solidus relations at 10, 15, and 20 kbar, determined and discussed in detail by *Boettcher and Wyllie* [1968*a*], were incorporated. Dashed lines are drawn where interpretation is uncertain.

The subsolidus mineral assemblage at crustal pressure corresponds to that of the natural rock, two feldspars, quartz, and a trace of biotite. At high pressures, for temperatures just below the solidus and with between 25 and 50 wt % H_2O, the subsolidus mineral assemblage is jadeite + coesite + kyanite. The change is caused by the breakdown of plagioclase to yield jadeite + quartz at about 17 kbar [*Boettcher and Wyllie*, 1968*b*]; by the transition of quartz to coesite at about 27 kbar [*Kitahara and Kennedy*, 1964]; by the disappearance of orthoclase and biotite at about 18 and 8 kbar, respectively, which is due to their solution in the large percentage of vapor [*Boettcher and Wyllie*, 1968*a*; *Piwinskii*, 1973; see discussion below for relationships with less H_2O]; and by the appearance of kyanite. No kyanite was found in a reexamination of the run products at 20 kbar of *Boettcher and Wyllie* [1968*a*]. The formation of kyanite might be expected to result in part from the breakdown of biotite and the anorthite component of the plagioclase, but the kyanite boundary is separated from those for biotite and plagioclase, and the presence of kyanite is probably due more to the preferential solubility of alkalis in the vapor as compared to alumina and possibly silica (see discussion below for H_2O-undersaturated conditions).

The solidus is identical (within the limits of experimental error) with that determined for a muscovite-granite by *Huang and Wyllie* [1973] and the melting curve for the eutectic and liquidus minimum in the system Ab-Or-Qz-H_2O [*Merrill et al.*, 1970; *Huang and Wyllie*, 1975]. The muscovite-granite solidus at 35 kbar is somewhat higher than the other two. The solidus determinations of *Boettcher and Wyllie* [1968*a*] are consistent with Figure 1 at 25 kbar, but somewhat higher in temperature at 30 kbar. Below 17-kbar pressure, increasing solubility of H_2O in the silicate liquid with increasing pressure lowers the solidus temperature. At about 17 kbar the solidus passes through a minimum and begins to increase in temperature with increasing pressure. This kind of change has been predicted through consideration of progressive change in the values of the partial molar volume of H_2O in vapor and liquid

phases [for example, discussion by *Carmichael et al.*, 1974], but in this example it is evidently due to the breakdown of plagioclase and the formation of the dense assemblage jadeite + quartz, as discussed by *Boettcher and Wyllie* [1967].

At 3 kbar, plagioclase is the liquidus mineral [*Piwinskii*, 1968*a*]. Between 5 kbar and 20 kbar, quartz is the liquidus mineral. At higher pressures, quartz (or coesite above 28 kbar) and kyanite occur together on the liquidus for H_2O-saturated liquids, but for higher H_2O contents, kyanite is the liquidus mineral (see Figure 2).

The liquidus boundary with excess H_2O has been reversed with 50°C brackets for quartz at 15 kbar (run 60, Table 2) and for quartz and kyanite at 22.5 kbar (run 44, Table 2). *Huang and Wyllie* [1973] reported pairs of runs reversing the corresponding liquidus boundaries in a muscovite-granite within 25°C brackets for quartz and kyanite at 15 and 25 kbar respectively. Water at pressures greater than 10 kbar has a remarkable kinetic effect on silicate reactions, as demonstrated for granite-H_2O systems at 10 kbar by *Piwinskii and Martin* [1970]. These facts suggest that the phase boundaries above 10 kbar in Figure 1 are not far from their equilibrium positions, but proof of this in multimineral felsic systems is extraordinarily difficult.

At pressures below 5 kbar, the melting interval is narrow, and the granite behaves as a eutectic-like composition. This is consistent with the fact that its composition, projected onto the system Ab-Or-Qz, is not far removed from the quartz-feldspar cotectic boundary for low pressures. The melting interval increases significantly at pressures above 5 kbar; it is 35°C at 2 kbar, 100°C at 10 kbar, and 150°C at 35 kbar. This is caused by the increasing temperature of the quartz-out curve and is consistent with change of the minimum-melting composition in the Synthetic Granite System, Ab-Or-Qz, away from SiO_2 towards $NaAlSi_3O_8$, both with excess H_2O and in the dry system [*Luth et al.*, 1964; *Luth*, 1969; *Huang and Wyllie*, 1975].

Phase Relationships With Variable H_2O Content

Figure 2 shows the phase relations determined at 30 kbar with varying weight percentages of water and interpolated to estimated results for the anhydrous rock composition (Tables 2 and 3). Phase boundaries are labeled through the melting interval. Figures 3*a* and 3*b* show similar, but less detailed, diagrams for results at 25 and 35 kbar, respectively, with dashed-line boundaries estimated according to determinations in Figures 1 and 2 (Tables 2 and 3). The granite itself contains 0.35 wt % H_2O, mostly in biotite, and this rock composition plots at
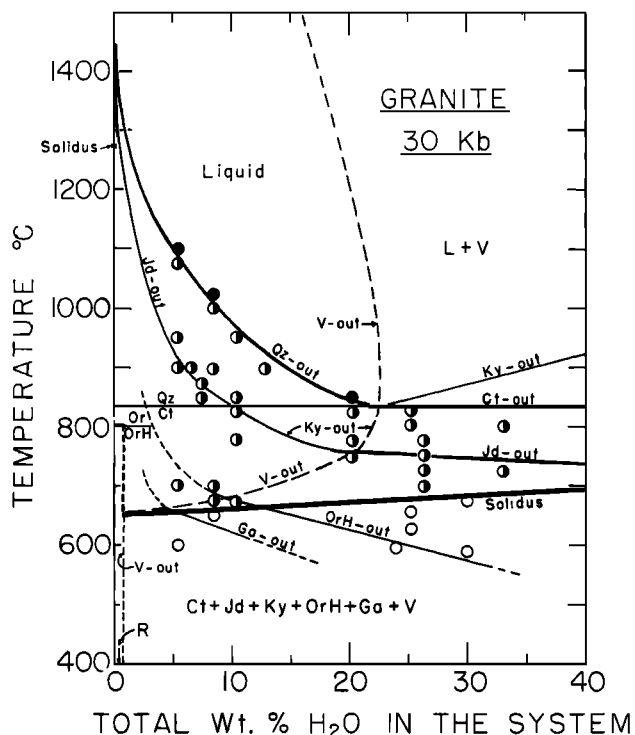
Fig. 2. Phase relationships for granite #104 with varying H_2O contents at 30 kbar. Definitive runs are listed in Tables 2 and 3. R on the horizontal axis represents the composition of the granite (0.35% H_2O contained in biotite). For abbreviations, see Figure 1, and OrH = orthoclase-hydrate, Ga = garnet.

the point marked R. The excess H_2O runs at 25, 30, and 35 kbar shown in Figure 1 are the runs plotted in Figures 2, 3a, and 3b with between 25 and 40 wt % H_2O (Table 2).

The H_2O-saturation boundary (V-out, Figure 2) separates the phase fields wth vapor present from those with vapor absent. The position of this boundary has not been experimentally determined but its approximate position is known from the analysis of *Robertson and Wyllie* [1971]. In runs from all fields labeled vapor present, there are deposits from the quenched vapor. Similar deposits also occur in some runs from the vapor-absent areas, and we believe that these derive from vapor that exsolved from liquid during the quench, as discussed above in connection with cavities in quenched glass. The process was discussed by *Boettcher and Wyllie* [1968a], and interpretation of the observed products in similar systems at lower pressures was reviewed in detail by *Whitney* [1975a].

For low H_2O contents (<5%) or low temperatures in the subsolidus region, which minimizes the effects of the solution of solids in the vapor, the high-pressure subsolidus assemblage is jadeite + coesite + kyanite + orthoclase-hydrate + garnet (Figure 2). This assemblage results from the subsolidus reactions discussed for H_2O-excess conditions and, in addition, the transition of orthoclase to orthoclase-hydrate [*Seki and Kennedy*, 1964] and the breakdown of biotite to produce garnet.

At low pressures the vapor phase composition is almost pure H_2O, but with increasing pressure, increasing amounts of rock dissolve in the vapor (see Figure 4). The high solubility of solids in the vapor at 30 kbar is indicated by the subsolidus disappearance of orthoclase-hydrate (Figure 2). Granite 104 contains 29% orthoclase, all of which presumably would form orthoclase-hydrate, given enough H_2O. At a given temperature the amount of orthoclase-hydrate, as determined from

the relative strengths of X ray peaks, decreases with increasing amounts of H_2O until it disappears. At 590°C it disappears with 27% H_2O. The phase relationships show that all K_2O has dissolved in vapor at this stage, but we cannot determine the distribution of Al_2O_3 and SiO_2 between vapor and residual minerals. The limited data available indicate that the solution reaction is strongly dependent on temperature (Figure 2).

The subsolidus dissolution of 29% alkali feldspar, congruently or incongruently, indicates that at pressures of 15 kbar and above (Figure 1) the aqueous fluids coexisting with granitic materials are very concentrated solutions [*Boettcher and Wyllie*, 1968a; *Stern and Wyllie*, 1973a]. The position of the boundary in Figure 3a limiting the subsolidus existence of alkali feldspar is assumed to be similar to that for orthoclase-hydrate at 30 kbar (Figure 2). Solution in the vapor phase also limits the subsolidus field of garnet (Figure 2). Preferential solubility of alkalis compared with alumina and possibly silica is shown by the development of an increasing area of kyanite stability with increasing H_2O content in the vapor-present region (Figures 2, 3a, and 3b). A segment of the kyanite-out curve (Figure 2) is drawn coincident with the saturation boundary. This curve connects the determined kyanite-out curves in the vapor-present region and in the vapor-absent region (which is coincident with the jadeite-out curve within experimental limits of detection).

At low pressures, where the vapor-phase composition is nearly pure H_2O, the phase boundaries for vapor-present conditions are isothermal. At high pressures, where the vapor is a concentrated solution, these phase boundaries are not isothermal, although this may not be detectable within the limits of experimental measurement [*Robertson and Wyllie*, 1971]. Figures 2, 3a, and 3b show that in the system granite-H_2O at 25 kbar or higher pressure, the vapor-present phase boundaries do depart measurably from isothermal lines. At 30 kbar the solidus rises 25°C between 8% and 25% H_2O; at 30 and 35 kbar the quartz-out and coesite-out curves drop 25°C between 25% and 50% H_2O; and at 35 kbar the jadeite-out curve drops 25°C between 25% and 50% H_2O.

There are three solidus reactions shown in Figure 2, depending on the amount of water present. In an anhydrous rock containing no hydrous minerals, the solidus is high, near 1250°C, as estimated from the results of *Luth* [1969] and *Huang and Wyllie* [1975] in the dry synthetic granite system. *Green and Ringwood* [1968] estimated 1300°C for the anhydrous solidus temperature of a rhyolite with 70% silica at 30 kbar. For low H_2O contents (0.7%) all H_2O may be structurally bound in orthoclase-hydrate, and the beginning of melting would be the temperature on the breakdown of orthoclase-hydrate, near 800°C at 30 kbar [*Huang and Wyllie*, 1974]. For a rock with more than 0.7% H_2O and a free vapor phase, the solidus is between 660° and 690°C, depending on the H_2O content, as discussed bove.

In the vapor-absent region the upper stability temperature of quartz, jadeite, kyanite, orthoclase-hydrate, and garnet increase with decreasing H_2O content. The phase boundary for quartz has been reversed within a 25°C bracket at 30 kbar with 12.5% H_2O (run 200, Table 3). The estimated liquidus temperature for the anhydrous granite is taken from *Green and Ringwood* [1968].

For a rock containing 5% H_2O at 30 kbar, melting begins at 670°C, garnet having already dissolved in the vapor phase just below the solidus. A few degrees above the solidus, the H_2O is completely dissolved in the liquid. With increasing

TABLE 3. Definitive Experimental Runs for Granite #104 With Amounts of Water Less Than Required to Saturate the Liquid

Run	Pressure, kbar	Temperature, °C	Water Added, wt %	Time, hours	Phases Present
109T	25	595	20	6	—
		825	—	15	L
108T	25	595	20	6	—
		850	—	21	L
107T	25	595	20	6	—
		875	—	12	L, (V)
100T	25	595	18	6	—
		800	—	16	Qz, L
113T	25	595	16	6	—
		850	—	18	Qz, L
112T	25	595	16	6	—
		875	—	14	L
111T	25	595	16	6	—
		900	—	14	L
229	25	595	6	6	Qz, Jd, Ky, Or, Ga, V
129	25	1000	6	6	Qz, L
133	25	1040	6	8	L
294	30	590	24	12	Ct, Jd, Ky, OrH, V
220T	30	590	20	6	—
		750	—	14	Ct, Jd, Ky, L
217T	30	590	20	6	—
		775	—	14	Ct, (Ky), L
187	30	825	20	11	Qz, L
186	30	850	20	11	L
200R	30	1050	12.5	6	—
		900	—	14	Qz, L
297T	30	590	10	4	—
		675	—	12	Ct, Jd, Ky, OrH, L, V
191T	30	590	10	6	—
		775	—	12	Ct, Jd, Ky, L, V
193T	30	590	10	6	—
		825	—	12	Ct, Jd, Ky, L
212T	30	590	10	6	—
		850	—	14	Qz, L
192	30	950	10	12	Qz, L
242T	30	590	8	6	—
		650	—	6	Ct, Jd, Ky, OrH, V
297T	30	590	8	4	—
		675	—	12	Ct, Jd, Ky, OrH, L, V
244T	30	590	8	6	—
		700	—	6	Ct, Jd, Ky, L
195T	30	590	8	6	—
		900	—	14	Qz, L
196	30	1000	8	8	Qz, L
198	30	1025	8	8	L
208T	30	590	7	6	—
		850	—	14	Qz, Jd, Ky, L
203T	30 ·	590	7	6	—
		875	—	14	Qz, Jd, Ky, L
209T	30	590	6	6	—
		900	—	14	Qz, L
236	30	590	5	6	Ct, Jd, Ky, OrH, Ga, V
299T	30	590	5	5	—
		700	—	12	Ct, Jd, Ky, OrH, L
298T	30	590	5	5	—
		900	—	6	Qz, Jd, Ky, L
201	30	950	5	12	Qz, L
214	30	1075	5	8	Qz, L
194	30	1100	5	8	L
103T	35	585	25	6	—
		825	—	14	Ct, Ky, L, V
114T	35	585	25	6	—
		850	—	14	L
98T	35	585	25	6	—
		890	—	14	L, V
66	35	585	22.5	6	Ct, Jd, Ky, V
86T	35	585	22.5	6	—
		690	—	14	Ct, Jd, Ky, V
83T	35	585	22.5	6	—
		720	—	14	Ct, Jd, Ky, L, V

Table 3. (continued)

Run	Pressure, kbar	Temperature, °C	Water Added, wt %	Time, hours	Phases present
75T	35	585	22.5	6	—
		745	—	14	Ct, Jd, Ky, L, V
74T	35	585	22.5	6	—
		765	—	14	Ct, Jd, Ky, L, V
115T	35	585	22.5	6	—
		785	—	14	Ct, Jd, Ky, L, V
124	35	900	22.5	8	L
125	35	900	20	8	Ct, L
120	35	975	14	11	Ct, L
121	35	1025	12.5	8	L

All runs conducted in Pt capsules. Abbreviations and symbols as in Table 2 and Ga, garnet; Or, ortho-clase; OrH, orthoclase-hydrate; ( ) indicates trace amounts.

temperature, first, orthoclase-hydrate, then jadeite and kyanite, and finally quartz, at 1090°C, dissolve in the liquid. Equilibrium crystallization of a granite liquid containing 5% dissolved H_2O proceeds in exactly the reverse sequence, with a free vapor phase separating from the liquid only at a very late stage of crystallization.

The liquidus boundary changes slope at its point of intersection with the vapor-saturation boundary, and this point gives the solubility of H_2O in the liquid [Robertson and Wyllie, 1971]. We have determined the position of the change in slope of the liquidus in Figures 2, 3a, and 3b as a measure of H_2O solubility. Figure 4 shows the solubility of H_2O in a granite liquid with increasing pressure, as determined from these diagrams and previously published results up to 8 kbar [Clark, 1966], as well as previously published results for the solubility of H_2O in basaltic and andesitic liquids and in the eutectic composition in the Residua System up to 8 kbar. The solubility of albite in aqueous vapor up to 10 kbar is also given. The high-pressure results are consistent with the approximate values and limits determined for albite composition by Boettcher and Wyllie [1969]. The brackets are wide, but they demonstrate that solubility of H_2O in granite liquids is limited with increasing pressure. Complete miscibility between liquid and vapor has been reported in the system SiO_2-H_2O at pressures above the second critical endpoint near 10 kbar [Kennedy et al., 1962], but the results in Figures 2, 3a, 3b, and 4 show that a miscibility gap persists between H_2O-saturated granite liquid and aqueous vapor at least to 35 kbar. The solubility relationships in silicate magma-H_2O systems thus appear to correspond more closely to the type predicted by Smith [1963, Figure 12-35] than to the type with critical endpoints, at least to mantle depths of 120 km, as discussed by Boettcher and Wyllie [1968a].

The H_2O-Undersaturated Liquidus Surface

Figure 5 shows the H_2O-undersaturated liquidus surface for the granite, extending from the dry liquidus (estimated from Green and Ringwood [1968]) to the H_2O-saturated liquidus (from Figure 1). The H_2O content of the saturated liquid increases from 0% at 1 bar to 27% at 30 kbar, as shown in Figure 4.

The surface is contoured by lines of constant H_2O content drawn from the known points on the excess-H_2O boundary (Figure 4) through corresponding points on the liquidus boundaries determined from the rock-water isobars at 15, 25 (Figure 3a), 30 (Figure 2), and 35 kbar (Figure 3b). The values at 15 kbar are consistent with results of Huang and Wyllie

[1973] for a muscovite granite. The map of the surface in P-T-X_{H_2O} space shows the fields for the liquidus and near-liquidus minerals based on the results shown in Figures 1, 2, 3a, and 3b, and it takes into account the results of H_2O-deficient experiments on similar compositions below 10 kbar [Eggler and Burnham, 1973; Whitney, 1975a]. Kyanite, a minor accessory mineral in Figures 1, 3, 3a, and 3b has been omitted from Figure 5 because kyanite does not appear on the liquidus for H_2O-under-saturated conditions (Figures 2, 3a, and 3b). Although the positions of the boundaries and the shape of the liquidus surface in Figure 5 may change with changes in some chemical parameters, the relative positions of the phase boundaries are correct for most rocks called granites and rhyolites. As far as the major minerals are concerned, the liquidus for all H_2O contents is dominated at high pressure by quartz or coesite and at pressures below 10 kbar corresponding to crustal depths, by quartz and plagioclase.

DISCUSSION

The phase relationships for a single rock summarized here provide constraints about its origin, but they do not provide an adequate basis for detailed discussion of the petrogenesis of I-type granitoids. It is necessary to consider, in addition, the phase relationships of the other rocks constituting a batholithic series as well as the field relationships and the geochemistry of trace elements and isotopes.

The phase relationships can be used to determine the conditions under which granite #104 could be a primary magma form various source rocks. The near-liquidus minerals for a primary magma must correspond to major minerals in the source rock at the depth and temperature of origin. The liquidus mineralogy of the granite is dominated by quartz or coesite at pressures above about 10 kbar (Figure 5), and no other mineral crystallizes through a considerable temperature interval below the liquidus (Figures 1, 2, and 3). The only candidates for source rocks above 10 kbar are mantle peridotite, subducted oceanic crust, and deep continental crust. Neither of the first two potential source rocks could yield granite liquid and residual quartz or coesite, and there are few deep crustal rocks likely to leave residual quartz. At pressures below 10 kbar, quartz on the liquidus is joined or replaced by plagioclase (Figures 5 and 1), and this is consistent with derivation of the granite liquid by partial fusion of continental rocks of varied composition.

The eutecticlike character of granite #104 with excess H_2O exists only up to pressures of about 5 kbar (Figure 1). At higher pressures the melting interval increases, indicating that
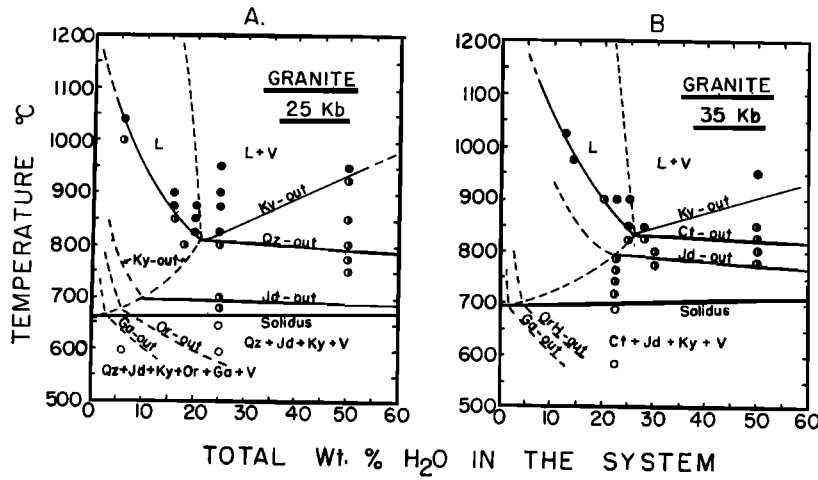
Fig. 3. Phase relationships for granite #104 at 25 and 35 kbar, with varying H_2O contents. Definitive runs are listed in Tables 2 and 3. Symbols and abbreviations as in Figures 1 and 2.

the compositions of liquids produced by partial melting of rocks of granitic composition depart progressively from the low-pressure eutectic composition. This has been demonstrated in synthetic systems [*Luth et al.*, 1964; *Luth*, 1969; *Huang and Wyllie*, 1975]. Therefore, we would not expect liquids of granite composition to be derived by partial melting of quartzo-feldspathic rocks at very high pressures.

The eutecticlike character of granite exists only for the conditions of excess H_2O. If there is less H_2O present than that required to saturate the liquid, there is a wide temperature interval for crystals plus liquid between liquidus and solidus. Figures 2 and 3 illustrate the phase relationships for high pressures, and the same general picture exists at lower crustal pressures [*Robertson and Wyllie*, 1971; *Whitney*, 1975a]. This is illustrated in Figure 6 for another biotite granite studied by *Maaløe and Wyllie* [1975] at 2 kbar. The melting interval with excess H_2O at 2 kbar is higher than that for granite #104 (Figure 1) because the ratio of plagioclase/quartz is higher. The interval between solidus and liquidus for H_2O content of 1% is

about 400°C, and H_2O-undersaturated liquid coexists with quartz, plagioclase, and alkali feldspar through 200°C. Considering source rocks with realistically low proportions of aqueous pore fluid, it is evident that this fluid dissolves within a few degrees of the solidus. Note in Figure 6 that without aqueous pore fluid, the solidus temperature of the biotite granite is considerably higher. Melting begins where biotite reacts to release H_2O for the liquid phase. The normal product of partial fusion of a wide range of crustal rocks is H_2O-undersaturated granite liquid [*Piwinskii and Wyllie*, 1970; *Brown and Fyfe*, 1970; *Robertson and Wyllie*, 1971; *Wyllie*, 1977a].

According to Figure 5, granite #104 at 40-km depth would be completely liquid at 1000°C with 2% H_2O, and at 860°C with 5% H_2O. Therefore, primary garnite melts with moderate H_2O contents could be generated in the crust at temperatures attained during regional metamorphism [*Turner*, 1968]. These magmas could reach near-surface levels before vesiculating where their paths crossed the excess-H_2O boundary (Figure 5).
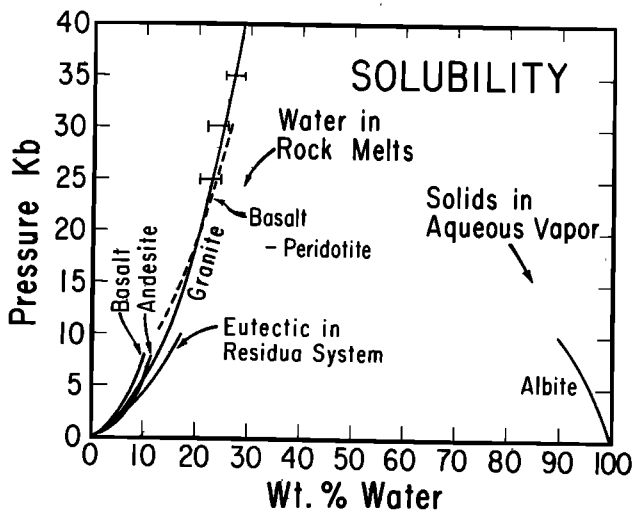

Fig. 4. The solubilities of H_2O in silicate liquids at the liquidus and of dissolved solid components in aqueous vapor, as a function of pressure. Brackets for the solubility in granite at 25, 30, and 35 kbar are from the experimental data in Figures 2, 3a, and 3b. The curve for basalt-peridotite is from *Green* [1973]. The data below 10 kbar are from the compilation by *Clark* [1966].
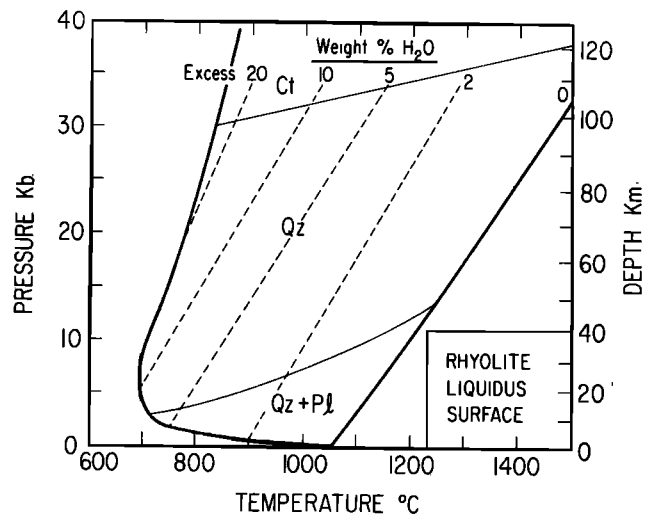

Fig. 5. The H_2O-undersaturated liquidus surface for granite #104 (rhyolite liquidus surface) connecting the H_2O-saturated liquidus (from Figure 1) with the dry liquidus. The surface is contoured by lines of constant H_2O content and mapped with areas of liquidus and near-liquidus minerals.
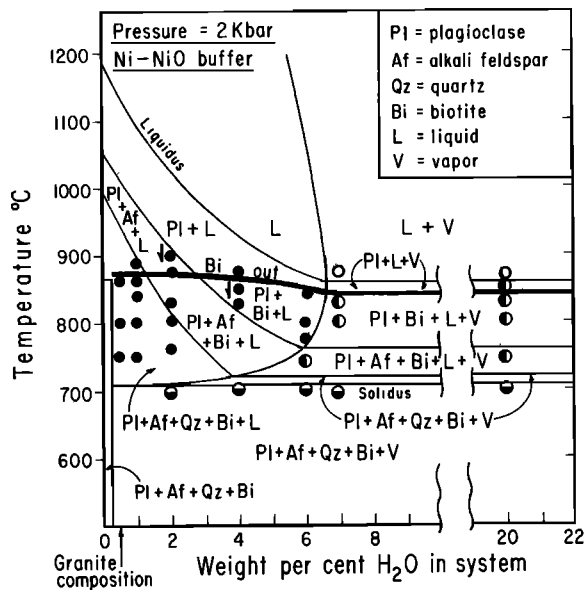
Fig. 6. Phase relationships for a biotite granite with varying H_2O contents at 2 kbar, with oxygen fugacity buffered [*Maaløe and Wyllie*, 1975]. Note the boundary between the phase fields with vapor and those without vapor (run circles filled). The heavy line is the upper stability limit of biotite, which intersects the phase boundaries for quartz and the feldspars in the vapor-absent region.

Maaløe and Wyllie [1975] concluded on the basis of granite petrography and experiments that most large bodies of granitic magma initially contained relatively low H_2O contents, probably less than 1.5%, and that most batholiths remained H_2O-undersaturated through most of their histories. H_2O-saturation and evolution of vapor occurs either as a result of uprise to lower pressures (Figure 5; *Whitney* [1975b]) or through crystallization (Figure 6; *Jahns and Burnham* [1969]). *Robertson and Wyllie* [1971] pointed out that although most granitic magmas evolve aqueous vapors only in the late stages of crystallization, insoluble volatile components, such as CO_2, may be concentrated in a vapor phase at an earlier stage together with a small proportion of H_2O. The consequences of this behavior were explored by *Holloway* [1976].

It has been established in experimental studies on granitoid rock sequences tonalite-granodiorite-granite-H_2O that the rocks consist of two groups of minerals with different characteristics. The minerals of the residua system, quartz, orthoclase, and the sodic portion of plagioclase feldspar melt together to produce a euteticlike granite liquid that coexists with the more refractory assemblage of calcic plagioclase, biotite, and amphibole, with little exchange of components among coexisting phases through a wide temperature interval [*Piwinskii*, 1968a, 1973; *Piwinskii and Wyllie*, 1968, 1970; *Gibbon and Wyllie*, 1969]. A wide range of granitoid magmas can be developed by combinations of granite liquid and suspended minerals of the more refractory group. The mafic inclusions in many batholiths are composed of the refractory mineral group with compostions consistent with the hypothesis that the magmas represent mixtures of granite liquid and residual minerals from the source rocks [e.g., *Piwinskii*, 1968b]. The designation of granite #104 as a eutecticlike granite liquid of I-type is based on the association of granite #104 with I-type granodiorities and tonalites [*Piwinskii*, 1968a, 1973].

For more detailed reviews of these and other experimental results relevant to the I-type granitoid series, including the

phase relationships of amphibole in the rocks and some discussion of the involvement of material from mantle and subducted oceanic crust, see *Piwinskii and Wyllie* [1968], *Stern et al.* [1975], *Wyllie et al.* [1976], *Wyllie* [1977a, b], and *Stern and Wyllie* [1978].

Johannes [1980] presented detailed studies on melting reactions in the synthetic granite system with excess H_2O at 5 kbar and raised an important question. To what extent is it valid to apply metastable experimental results to natural processes? He reviewed some of the previous attempts to test for equilibrium in experiments on similar systems. He concluded that overinterpretation of granitic systems should be carefully avoided and that controversies about the formation of granites and migmatites are due to contradictory experimental data and inconsistent interpretations of the data. Johannes' results indicate that solidus curves determined for crystalline materials with excess H_2O are close to equilibrium but that other melting curves may be considerably below stable temperatures. He demonstrated that plagioclase of intermediate composition melts almost stoichiometrically, producing too much liquid enriched in $(Ca + Al)/(Na + Si)$ compared with the equilibrium amount and composition. Under these conditions the whole system is metastable, and the positions of phase boundaries for other minerals must also be metastable. He estimated that it would take 10^{14} years to reach compositional equilibrium at 665°C. Therefore, he concluded, the separation of melts with metastable compositions may occur during anatexis, just as the occurrence of zoned plagioclase illustrates disequilibrium between plagioclase and melt during crystallization.

We agree that the attainment and demonstration of reversible equilibrium within narrow temperature intervals in many parts of multimineral granitic systems is impossible [*Stern and Wyllie*, 1975; *Wyllie*, 1977b]. From our experience with granitic systems at crustal pressures we would consider any applications claiming to use precise temperatures or compositions of feldspars and liquid to be suspect because of the clear evidence that equilibrium values cannot be attained experimentally [*McDowell and Wyllie*, 1971; *Johannes*, 1980].

Reaction rates improve with increasing temperature, with increasing pressure in the presence of H_2O, and in PT regions where feldspars are unstable. Note the two-stage runs required at pressures above 15 kbar to remove feldspar from the starting material in order to avoid metastable melting (Table 2). Even at high pressures, the demonstration of reversible brackets narrower than 50°C is difficult [*Stern and Wyllie*, 1975]. In general it appears that the phase relationships best approaching equilibrium conditions are at the solidus and near the liquidus. At crustal pressures, particularly within the vapor-absent region, details of the phase relationships within the crystallization interval are unreliable. Conditions are greatly improved at pressures above about 15 kbar, but there are many examples of metastability at temperatures below 800°–900°C.

We endorse *Johannes'* [1980] conclusion and hope that we do not overinterpret our data. Metastable conditions are most prevalent in the H_2O-undersaturated region illustrated in Figure 6, the region most applicable to natural granites. Because the phase compostions in experiments are certainly not equilibrium values, the positions of the phase boundaries are not precisely located. Only the biotite-out boundary could be reversed [*Maaløe and Wyllie*, 1975], but because the liquid composition was metastable, even the biotite phase boundary

could represent metastable equilibrium. However, from the available experimental data and interpolation between dry and excess-H_2O conditions [*Robertson and Wyllie*, 1971], it is evident that the general pattern illustrated in Figure 6 is valid. To that extent it is appropriate to draw petrogenetic conclusions about processes and changes in sequence of crystallization as a function of changes in H_2O content. Overviews of the phase relationships for series of related granitic rocks [e.g., *Piwinskii*, 1968a, 1973; *Piwinskii and Wyllie*, 1968, 1970; *Gibbon and Wyllie*, 1969] illustrate sufficient consistency, within a given series and from one series to another, that we feel confident in the broad pattern of phase relationships that emerges, which we have applied in the cited papers and outlined above.

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