Phase relationships of gabbro-tonalite-granite-water at 15 kbar with applications to differentiation and anatexis

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ABSTRACT

Phase relationships have been determined at 15 kbar with variable H₂O contents for three rocks—a gabbro, a tonalite, and a muscovite granite—representing the compositional trend of the calc-alkaline rock series. Experiments were conducted in 0.5-in. piston-cylinder apparatus using Ag-Pd or Pt capsules. The results obtained are acceptable representations of the phase relationships for elucidation of petrological processes. Selected runs with 5% H₂O were completed using Au capsules to overcome the problem of iron loss, up to the temperature limit of Au, for reliable electron microprobe analyses of glass, garnet, clino-pyroxene, amphibole, and plagioclase. No glasses could be analyzed in the gabbro. The data provide K_D values as a function of the evaluate (1) the fractionation trends in hydrous magmas at 55 km in thickened continental crust or uppermost mantle and (2) the products of anatexis of the thickened crust. At this depth, fractionation of hydrous basalt, or anatexis of gabbro and tonalite or their metamorphosed equivalents, appears to produce liquids diverging from the calc-alkaline trend. Anatexis of granite produces a liquid less siliceous than itself, with some chemical characteristics of syenite.

INTRODUCTION

One of the major chemical trends in igneous petrology is given by the calc-alkaline rock series gabbro-tonalitegranodiorite-granite (basalt-andesite-rhyolite). The phase relationships of specific rocks in this series have been studied under a variety of conditions by many investigators, commonly with applications to particular petrogenetic problems related to the specific rocks. The experimental results for three rocks at 15 kbar are presented in this paper in $T-X_{H_{2O}}$ phase diagrams, together with a set of reliable analyses of minerals and glasses.

The more general construction of the phase relationships for the complete rock series, representing a compositional line through the components of igneous rocks, has been addressed by Piwinskii and Wyllie (1968, 1970) and Piwinskii (1968, 1973a, 1973b, 1975) with excess H₂O at 2 and 10 kbar, by Green and Ringwood (1968) for the anhydrous series at 18, 27, and 36 kbar [see also Green (1972), Green and Ringwood (1972) for the effect of H₂O on the liquidus at high pressures], by Stern and Wyllie (1973, 1978) at 30 kbar with H₂O contents from 5% to excess, and by Green (1982) at 15 and 30 kbar from dry to excess H_2O . An important petrogenetic question is to what extent the liquid compositions within the crystallization intervals of gabbro and tonalite parallel the calc-alkaline composition trend, for a variety of pressures and water contents.

EXPERIMENTAL METHODS

Starting materials

Natural olivine tholeiitic basalt (gabbro), tonalite, and muscovite granite were used as starting materials. The chemical compositions, CIPW norms, and approximate modes are listed in Table 1. The tholeiite is from a fine-grained basaltic sill in Scotland (Lambert and Wyllie, 1972). The tonalite from the Sierra Nevada batholith was kindly provided by P. C. Bateman and F. C. Dodge (tonalite 101, or M 127 in Piwinskii, 1973b). Field and petrographic descriptions of the tonalite have been given by Bateman et al. (1963). The granite collected from Harney Peak, South Dakota, was kindly provided by T. T. Norton and R. T. Mc-Laughlin of the U.S. Geological Survey (Huang and Wyllie, 1973, 1981). The chemistry of major elements in these rocks corresponds closely to the calc-alkaline trend (although the granite is of S-type).

Apparatus and procedures

Experiments were performed in a single-stage piston-cylinder apparatus similar to that described by Boyd and England (1960), using a 0.5-in.-diameter piston and chamber with hardened steel liner. The apparatus was calibrated for pressure and temperature as described by Boettcher and Wyllie (1968). Temperatures, measured with chromel-alumel (below 850°C) and Pt-Pt₉₀Rh₁₀ (above 850°C) thermocouples, were precise to \pm 5°C and accurate to \pm 15°C. Furnace assemblies were constructed from graphite and talc for runs up to 850°C, but for higher temperatures, the talc rods were replaced by pyrex glass to avoid talc dehydration and Run

Temperature

Table	1.	Chemical	analyses,	CIPW	norms	and	approxim	ate
	m	odes for w	hole rocl	cs in th	he pres	ent s	study	

Table 2. Results of quenching experiments for gabbro (DW-1) at 15-kbar pressure

Time

hour Rune Veing F Results

	Gabbro, DW-1	Tonalite 101	Granite L26
(1) Chemical analyses			
Si0,	45.91	59.14	74.66
TiO2	0.94	0.79	0.03
A1203	17.19	18.23	15.55
Fe ₂ O ₃	2.33	2,32	0.17
FeO	7.67	3.62	0.42
MnO	0.22	0.11	0.07
MgO	7.48	2.50	0.02
CaO	13.54	5.92	0.42
Na ₂ 0	1.63	3.81	4.29
K20	0.14	2.19	3.08
H20+	1.78	0.82	0.66
H20-	1.26	0.04	0.04
P205	0.04	0.30	0.15
C02	nil	0.01	0.02
(2) CIPW Norms			
Quartz	_	11.7	37.16
Orthoclase	0.83	12.9	18.20
Albite	13.78	32.2	36.28
Anorthite	39.14	26.2	0.98
Diopside	22.59	0.9	
Hypersthene	6.95	9.4	
Olivine	8.55		
Magnetite	3.39	3.4	0.25
Ilmenite	0.78	1.5	0.06
Apatite	0.10	0.7	0.36
Corundum			4.80
(3) Approximate Modes			
Quartz		13	105 3
Alkali Feldspar		4.5	105.2
Plagioclase	47	59	
Augite	47		
Biotite		12.5	0.1
Hornblende		9	
Olivine	3		
Opaques	3	2)
Garnet			0.9
Apatite)
Muscovite			13.8

	4. 48.49	10		and the second second second
483	800	30	30	Cpx, Hb, L
481	825	4.4	23	Cpx, Hb, L
484	825	30	22	Cpx, Hb, L
451	850	30	11	Cpx, Hb, L
480	875	5	23	Cpx, Hb, Gt(?) + L
454	900	30	23.5	Cpx, Hb, L
453	925	5	34	Cpx, Hb, L
452	975	4.5	23	Cpx, Hb, L
456	1000	30	23.5	Cpx, Hb, L
455	1025	5	23	Cpx, Hb, L
457	1050	30	12	Cpx, Hb(tr), L
463	1050	40	12	Cpx, Hb(tr), L
467	1075	20	11	Cpx(tr) + L
168	1075	25	11	Cpx(tr) + L
470	1075	25	10	Cox(tr) + L
461	1075	30	18	T.
401	1075	40	13	T.
409	1075	40	14	Cov + L
472	1100	10	14	CDX 1 H
476	1100	10	22	
4/1	1100	15	23	L T
459	1100	30	14	
462	1125	5	23	Cpx(CI), L
460	1150	5	14	L .
458	1200	5	11	<u>L</u>
	"Singl	e-Stage <u>"</u> Kuns Usi	ng Ag-Pa ca	tpsules
488	1000	5	3	Cpx, Hb, Ga, L
486	1100	5	1	Cpx, HD(?), L
485	1150	5	1	Cpx(tr), L
		5	1	
487	1200			1/20
487	1200	o-Stage" Runs Usi	ng Pt-Capsi	1168
487	1200 "IW 1150	o-Stage" Runs Usi 40	ng <u>Pt-Capsi</u> 7	
487	1200 "7w 1150 1020	<u>o-Stage" Runs Usi</u> 40 40	<u>ng Pt-Capsi</u> 7 22	Cpx, Hb(?), L
487 473 466	1200 <i>"Tw</i> 1150 1020 1150	<u>o-Stage" Runs Usi</u> 40 40 40	<u>ng Pt-Capsi</u> 7 22 7	Cpx, Hb(?), L
487 473 466	1200 "Tw 1150 1020 1150 1040	<u>o-Stage" Runs Usi</u> 40 40 40 40 40	<u>ng Pt-Capsi</u> 7 22 7 25	Cpx, Hb(?), L Cpx, L
487 473 466 475	1200 <i>"Tw</i> 1150 1020 1150 1040 1200	<u>o-Stage" Runs Usi</u> 40 40 40 40 40 5	<u>ng Pt-Capsi</u> 7 22 7 25 9	Cpx, Hb(?), L Cpx, L
487 473 466 475	1200 1150 1020 1150 1040 1200 1050	<u>o-Stage" Runs Usi</u> 40 40 40 40 5 5 5	<i>ng Pt-Capsi</i> 7 22 7 25 9 25	Cpx, Hb(?), L Cpx, L Cpx, L
487 473 466 475 477	1200 1150 1020 1150 1040 1200 1050 1150	<u>o-Stage" Runs Usi</u> 40 40 40 40 5 5 15	ng Pt-Capsi 7 22 7 25 9 25 21	Cpx, Hb(?), L Cpx, L Cpx, L
487 473 466 475 477	1200 1150 1020 1150 1040 1200 1050 1150 1050	o <u>-Stage" Runs Usi</u> 40 40 40 40 5 5 15 15	ng Pt-Caper 7 22 7 25 9 25 21 24	Cpx, Hb(?), L Cpx, L Cpx, L Cpx, L Cpx, Hb(?), L
473 473 466 475 477 478	1200 1150 1020 1150 1040 1200 1050 1150 1150	0-Stage" Runs Usi 40 40 40 5 5 5 15 15 20	ng Pt-Caper 7 22 7 25 9 25 21 24 6	Cpx, Hb(?), L Cpx, L Cpx, L Cpx, L Cpx, Hb(?), L
487 473 466 475 477 478	1200 mTw 1150 1020 1150 1040 1200 1050 1150 1050 1150 1050	0-Stage" Runs Usi 40 40 40 5 5 15 15 15 20 20	ng Pt-Caper 7 22 7 25 9 25 21 24 6 23	Cpx, Hb(?), L Cpx, L Cpx, L Cpx, Hb(?), L Cpx, L
487 473 466 475 477 478 479	1200 1150 1020 1040 1200 1050 1150 1050 1150 1050 1150	0-Stage" Runs Usi 40 40 40 5 5 15 15 15 20 20 30	ng Pt-Capsi 7 22 7 25 9 25 21 24 6 23 9	Cpx, Hb(?), L Cpx, L Cpx, L Cpx, L Cpx, Hb(?), L Cpx, L
487 473 466 475 477 478 479	1200	o <u>-Stage" Runs Usi</u> 40 40 40 5 5 15 15 15 20 20 30 30	ng Pt-Lapsi 7 22 7 25 9 25 21 24 6 23 9 24	Cpx, Hb(?), L Cpx, L Cpx, L Cpx, Hb(?), L Cpx, L L
487 473 466 475 477 478 478 479 474	1200 - 726 1150 1020 1050 1050 1050 1150 1050 1150 1050 1150 1050 1200	o-Stage" Runs Usi 40 40 40 5 5 15 15 15 20 20 30 30 5	ng Pt-capel 7 22 7 25 9 25 21 24 6 23 9 24 11	Cpx, Hb(?), L Cpx, L Cpx, L Cpx, Hb(?), L Cpx, L L
487 473 466 475 477 478 478 479 474	1200 725 1150 1020 1150 1040 1050 1150 1050 1150 1050 1150 10	o <u>-Stage" Runs Usi</u> 40 40 40 40 5 5 15 15 20 20 20 30 30 5 5	ng Pr-capel 7 22 7 25 9 25 21 24 6 23 9 24 6 23 9 24 11 23	Cpx, Hb(?), L Cpx, L Cpx, L Cpx, Hb(?), L Cpx, L L L
487 473 466 475 477 478 479 479 474	1200 - 726 1150 1020 1150 1050 1050 1050 1050 1050 1050 1050 1050 1050 1050 1050 1200 1075 1200	o <u>-Stage" Runs Usi</u> 40 40 40 5 5 15 15 15 20 20 30 30 5 5 5	ng Pt-capel 7 22 7 25 9 25 21 24 6 23 9 24 11 23 7	Cpx, Hb(?), L Cpx, L Cpx, L Cpx, Hb(?), L Cpx, L L L

embrittlement. All runs were brought to final pressure with the "piston-out" procedures as described by Boyd et al. (1967). Pressures listed are nominal, incorporate no corrections for friction, and are considered accurate to $\pm 5\%$.

Crystalline rock samples were used in the experiments. Oxygen fugacity was not controlled. The oxidation state of the sample during the run conditions should be close to the Ni-NiO buffer (Allen et al., 1975). Water and (dry) powdered rock sample were weighed into capsules in the required proportions, sealed, and run at 15 kbar and selected temperatures. The run tables list the H₂O weighed into the capsules. The actual H₂O present in a capsule during a run was thus the total of H₂O stored in the hydrous minerals of the rock, plus the H₂O added. Two types of runs were made to determine the phase boundaries: (1) "singlestage" runs in which the crystalline rock samples were brought directly to the desired temperatures and (2) "two-stage" runs in which the crystalline samples were held above the liquidus until completely melted and then the temperature was reduced to the desired value. The first type was prevalently used in the present study while the second was made as a test for equilibrium.

Electron-microprobe analyses were performed on quenched charges at two intervals during the present study. Early reconnaissance analyses were made on an ARL/EMX electron-microprobe analyzer at 15 kV, 0.02 μ A sample current, for 10 s per element. The beam size was about 2 μ m. The microprobe analyzer was then automated. Most of the analyses for the present study were performed on the computerized ARL/EMX analyzer, using standard procedures for the J. V. Smith laboratory at the University of Chicago. The accuracy of analyses is $\pm 2\%$ of the amount of major elements present.

Identification of phases

Phases present in quenched runs were identified using standard optical and X-ray powder-diffraction techniques, described in previous papers on these rocks. Phases encountered include in the gabbro-water system, amphibole, clinopyroxene, garnet, liquid, and vapor deposits; in the tonalite-water system, garnet, clinopyroxene, plagioclase, quartz, biotite, liquid, and vapor deposits; in the granite-water system, quartz, plagioclase, alkalifeldspar, muscovite, kyanite, sillimanite, corundum, garnet, liquid, and vapor deposits. Opaque minerals, although of interest, were too sparse for confident identification.

EXPERIMENTAL RESULTS AT 15 KBAR

One major uncertainty in the interpretation of experimental results is the absorption of iron from samples by the noble-metal capsules (Merrill and Wyllie, 1973; Stern and Wyllie, 1975; Nehru and Wyllie, 1975). Experiments for the gabbro-water system were first performed using Pt capsules. In order to test the effect of iron loss on the liquidus boundary, some additional runs with 5% H_2O were performed, using $Ag_{75}Pd_{25}$ capsules to determine the liquidus temperature. Most runs for the tonalite-water system were made using $Ag_{30}Pd_{70}$ capsules. Runs for the low-iron granite-water system were performed using Pt capsules. When the phase diagrams had been determined, selected runs were com-



Fig. 1. Phase relations of gabbro (basalt) at 15 kbar with varying H_2O contents. For definitive runs and abbreviations, see Table 2. Squares indicate runs of Lambert and Wyllie (1972). See text for other data sources. H_2O bound in the original rock is indicated by the arrow. Only for 0% H_2O is mineral assemblage devoid of Hb \pm Bi. (Ga) indicates garnet, which should be stable, but failed to nucleate except in Au capsules (see text).

pleted in Au capsules for analysis of minerals and glasses with minimum iron loss, up to the temperature limit of Au.

Phase relationships for gabbro-water

Figure 1 shows the experimental results at 15 kbar for the melting relations of gabbro with 5–40% H_2O added. The H_2O structurally bound in the original rock is shown by the arrow. Near-solidus runs with excess H_2O are from Lambert and Wyllie (1972). The definitive runs are listed in Table 2. The liquidus temperature of an anhydrous rock of similar composition was determined by Green and Ringwood (1968). The solubility of H_2O in gabbro liquid at 15 kbar and 1080°C, which should be given by the change of the slope of liquidus boundary, is not constrained.

The subsolidus mineral assemblage at this pressure with excess water is Ga + Hb + Cpx + Pl + Qz + V according to the results of Lambert and Wyllie (1972). There are three solidus temperatures, depending upon the amount of water present. For a dehydrated rock, the solidus temperature is about 1200°C, esti-

mated from Green and Ringwood (1968). For a vapor-absent rock, with all H_2O stored in amphibole, the solidus corresponds to the reaction temperature of amphibole in this assemblage, extrapolated from runs with H_2O added. This temperature was not determined, but it is probably between 1000 and 1100°C. For a rock with a free vapor phase, the solidus is at 635°C.

Plagioclase and quartz disappear, respectively, at 15 and 40°C above the solidus in the presence of excess water. The upper stability boundaries for plagioclase and quartz are estimated by interpolation between the anhydrous melting relations of similar rock compositions (Green and Ringwood, 1968; Ito and Kennedy, 1968) and the melting boundaries in the presence of excess H_2O . The boundaries fall steeply with increasing H_2O in the vapor-absent region. The runs do not define the position of the dashed boundary separating the phase fields with vapor present or absent.

Amphibole is present from subsolidus temperature to nearliquidus temperature (1070°C) with excess H_2O . In the vaporabsent region, we expect the upper stability temperature of amphibole to increase slightly with decreasing H_2O content (Hol-



Fig. 2. Phase relations of tonalite at 15 kbar with varying H_2O contents. For definitive runs and abbreviations, see Table 3. Squares indicate runs from Lambert and Wyllie (1974). See text for subsolidus changes, other data sources, and see legend for Figure 1.

loway, 1973). No garnet was observed in run products using Pt and Ag-Pd capsules, except in a single run (#R488) at 1000°C with 5% H_2O (Ag₇₅Pd₂₅). Yet garnets occur in runs from Au capsules with 5% H_2O between 700 and 1000°C (Table 5). The failure of garnet to nucleate under these conditions is well known and much reviewed (Lambert and Wyllie, 1972, 1974; Green, 1972). The nucleation of garnet in Au capsules may be due to retention of iron in the sample. (Ga) indicates regions where garnet should be stable, despite its failure to nucleate in Pt and Ag-Pd capsules.

Clinopyroxene and garnet are the near-liquidus phases for all H_2O contents (separate boundaries not distinguished). They are joined by amphibole just below the liquidus with excess H_2O . Through more than 350°C, liquid coexists with amphibole, clinopyroxene, and garnet for H_2O contents at least down to 5%.

Phase relationships for tonalite-water

Figure 2 shows the experimental results at 15 kbar for the melting relations of tonalite with 5-35 wt% H₂O added. The H₂O structurally bound in the rock is shown by the arrow. Near-solidus

runs with excess H₂O are from Lambert and Wyllie (1974). The definitive runs are listed in Table 3. The liquidus temperature for anhydrous tonalite is near 1250°C as estimated from Green's (1972) study of a rock of similar composition. The liquidus temperature drops to about 1140°C for the vapor-absent rock (with H₂O released from amphibole and biotite), and down to 940°C with excess H₂O. The solubility of H₂O in tonalite liquid at 15 kbar and 950°C, which should be given by the change in slope of the liquidus boundary, is not constrained. Clinopyroxene and amphibole are liquidus or near-liquidus phases with excess H₂O. Clinopyroxene occurs only in minor amounts except near the liquidus. In the vapor-absent region, the upper stability temperature of amphibole changes little with decreasing H₂O content and therefore diverges from the liquidus. Amphibole is the dominant phase down to the solidus region. The biotite-out curve rises to somewhat higher temperatures in the vapor-absent region. Precise determination of the amphibole-out and biotite-out curves at low H₂O contents is highly desirable, but experimentally difficult.

The solidus at 15 kbar is within the garnet stability field and in the region of the reaction of plagioclase to jadeitic pyroxene. According to Lambert and Wyllie (1974), the subsolidus assemblage with excess H_2O is Pl + Qz + Hb + Bi, with a trace of Cpx and possible Ky, and with Ga, which failed to nucleate. Plagioclase should be replaced completely by clinopyroxene and garnet within a short temperature interval below the solidus. This is not indicated in Figure 2, and no runs were completed to establish this, but the general picture is clear (Lambert and Wyllie, 1974, Fig. 1). There are three different solidus reactions and temperatures, depending on H_2O content, as discussed for gabbro- H_2O .

Plagioclase disappears within 5°C above the solidus with excess H₂O, but is stable to considerably higher temperature, 950°C, with 5% H₂O added, and is stable to almost 1350°C in a dehydrated rock (Green, 1972). For a dehydrated andesite, quartz is stable to about 1150°C, 50°C below the liquidus (Green, 1972), but addition of 5% H₂O is sufficient to lower its upper stability temperature to about 775°C. Quartz disappears about 50°C above the solidus with excess H₂O. The dashed boundary separating vapor-absent from vapor-present fields is only estimated. However, its estimated position constrains the low-temperature ends and the curvatures of the plagioclase-out and quartz-out boundaries. The latter boundary has the normal concave-upward curvature (see Figs. 1 and 3). The unusual, retrograde shape for the plagioclase-out curve is a consequence of the plagioclase-clinopyroxene reaction near the solidus, which can be modeled in the system NaAlSiO₄-SiO₂-H₂O.

In the presence of excess vapor, trace amounts of garnet were observed at 15 kbar between 725 and 875° C by Lambert and Wyllie (1972). In the present experiments with Ag-Pd capsules, garnets were observed down to 850° C with 5% H₂O added. The amount of garnet increases with temperature, and near the liquidus, garnet and clinopyroxene become the dominant phases. However, garnet appears in runs down to 700°C in Au capsules with 5% H₂O (Table 5). The failure of garnet to nucleate at lower temperatures where it should be stable, denoted in Figure 2 by (Ga), was already discussed in connection with the gabbro-water system and by Lambert and Wyllie (1972).

Phase relationships for granite-water

Figure 3 shows the experimental results at 15 kbar for the melting relationships of muscovite-granite with and without water added, and the results are extrapolated toward the anhydrous rock composition (Huang and Wyllie, 1973, 1981). The H_2O structurally bound in the muscovite granite is shown by the arrow at 0.66%. The definitive runs are listed in Table 4. The subsolidus assemblage at this pressure corresponds to that of the natural rock, two feldspars, quartz, and muscovite, with just a trace of garnet.

The phase-boundary between vapor-absent and vapor-present fields is determined by runs in Figure 3, in contrast to Figures 1 and 2, and this gives a better estimate of H_2O solubility in the liquid at about 775°C. In the vapor-absent region, upper boundaries for quartz, feldspars, and garnet decrease considerably with increasing H_2O content. The muscovite-out temperature increases somewhat with decreasing H_2O content, as anticipated from phase relationships in synthetic mica systems (Yoder and Kushiro, 1969; Huang and Wyllie, 1974). The vapor-absent solidus for the beginning of reaction of Na-bearing muscovite in this assemblage has been measured (Huang and Wyllie, 1981).

Quartz was the liquidus phase for the biotite-granite studied by Stern and Wyllie (1973, 1981), and the corresponding boundary is shown by the heavy line in Figure 3. For the aluminous granite used in the present study, traces of corundum persisted

Table 3. Results of quenching experiments for tonalite (101)at 15-kbar pressure

lun	remperature	H ₂ U	Time	Results*
	"Sin	ale-Stage	" Runs Us	ing Aggo-Pdyo Capsules
38	750	5	14	Hb. CDx. Pl. Oz. Bio, Ky. L
44	800	5	15	Hb, Cpx, Pl, Bio, Ky, L
47**	825	5	9.6	Hb, Cpx, Pl, Bio, L
19	850	5	24	Hb, Cpx, Ga(tr), Pl, Bio(?), Ky(?), L
42	875	5	9	Hb, Cpx, Ga, Pl, Ky(?), L
13	925	5	12	Hb, Cpx, Ga, Pl, Ky(tr), L
41	925	5	3	Hb, Cpx, Ga, Pl, Ky(tr), L
03	925	33	13	Hb, Cpx(tr), Ky, L
22	940	32.7	11	L
20	940	50	7	L
129	950	20	20	Hb(tr), Cpx, Ky, L
104	950	20	21	Hb, Cpx, Ky(tr), L
23	950	28	18.5	L
112	975	5	7	Hb(?), Cpx, Ga, L
116	975	14.7	21.5	Cpx, L
127	975	23.3	9.5	L
117	1000	12	14	L
10.2	1000	33	5	L
114	1025	5	25	Cpx, L
1/5**	1025	5	3	Cpx, Ga, L
135	1025	5	3	Cpx, Ga, L
110	1050	5	6	L
108	1100	5	6	L
124	1225	0	5	Cpx, L
110	1150	ő	5	T.
121	1150	ů.	12	T.
107	1150	5	18	T.
105	1200	5	18	T.
10.5	"7	wo-Stage"	Runs Usi	ng Ag ₃₀ -Pd ₇₀ Capsules
120	1000	33	5	
:50	915	33	17	Hb(tr), Cpx, L
134	1050	33	9	
1.74	925	33	22	Cox, L
170	1050	23	6	apart -
120	950	23	18	L
125	1050	20.4	10	
125	965	20.4	35	Cpx(?), L
122	1050	13	17	aprillion ()
*)J	975	13	24	Cpx, L
122	1300	5	21	
3 J &	1000	5	25	Cox. L
121	1100	5	6	
*41	1025	5	14	L

For abbreviation see Table 2. Additional abbreviations: Ga = garnet; Pl = plagioclase; Bio = biotite; Ky = kyanite.

to higher temperatures. Metastable corundum forms from the breakdown of muscovite at 15 kbar, instead of the anticipated Al_2SiO_5 polymorph. Corundum, once formed metastably, persists indefinitely in this system, as well as in parts of the synthetic muscovite system (Huang and Wyllie, 1974).

Phase relationships for gabbro-tonalite-granite-water

Figure 4 compares and combines the phase relationships for the rock series at 15 kbar with 5% H₂O. The phase boundaries have been drawn through points transferred from Figures 1, 2, and 3. The data of Green and Ringwood (1972) on a rhyodacite with 69% SiO₂ were included in construction of the diagram. The diagram shows two liquidus piercing points bounding the garnet liquidus between about 60 and 70% SiO₂, with lowest liquidus temperature near 70% SiO₂. The effect of pressure and H₂O content on the liquidus profile for the calc-alkaline rock series has been discussed by Green and Ringwood (1968) and Stern and Wyllie (1973, 1978).

Test of equilibrium

The phase diagrams in Figures 1, 2, and 3 are reaction diagrams, with phase boundaries drawn on the basis of single-stage runs using capsules of Pt and $Ag_{75}Pd_{25}$ for gabbro, $Ag_{30}Pd_{70}$ for tonalite, and Pt for granite. Tests for continuation or completion of reaction and for the attainment of equilibrium include increasing run duration and making two-stage runs (also necessarily of longer duration) to reverse the reactions. The longer durations



Fig. 3. Phase relations of granite at 15 kbar with varying H_2O contents. For definitive runs and abbreviations, see Table 4. Modified after Huang and Wyllie (1973).

for enhancing the degree of reaction and testing reversibility introduce other problems, such as increased iron loss from the sample and contamination of thermocouple junctions, causing drift of temperature.

The liquidus boundaries for gabbro-water were determined in three groups of runs: (1) Pt capsules in single-stage, (2) Ag75Pd25 capsules in single-stage, and (3) Pt capsules in two-stage runs. The definitive runs are listed in Table 2. The liquidus boundary determined by the first group is at 1080°C with excess water. With 5% H_2O , the liquidus boundary is 1130°C, identical to that from the second group of runs. However, the liquidus boundary determined by two-stage runs is 55°C lower with 5% H₂O and 30°C lower with excess H₂O. For the tonalite-water system, the liquidus boundaries for clinopyroxene were reversed successfully in two-stage runs within a 25 and 50°C bracket, respectively, for 33 and 5% water contents; but no amphibole or garnet crystallized in these two runs in contrast with their presence in the singlestage runs. The difference between liquidus temperatures determined by single-stage and two-stage runs for both gabbro and tonalite is tentatively attributed to the nucleation problem, but also to the iron loss of bulk composition from charge to capsules. For the granite-water system, the upper boundary of quartz was experimentally determined with a 25°C bracket at 15 kbar with

excess water (runs 240 and 242 in Table 4) and with 9.5% water added at 25 kbar (runs 215 and 217; Huang and Wyllie, 1981). The granite-water system is notorious for its sluggish reaction rates. Although the results in Figures 1, 2, and 3 must be regarded as provisional, for the reasons stated above (similar statements could be made for most published rock-H₂O studies), the results with Au capsules (5% H₂O) are broadly consistent (Table 5). Therefore, the diagrams are considered to be acceptable representations of the phase relationships, with respect to major assemblages and geometrical sequences.

The effect of iron loss from the sample in changing the phase assemblage, in addition to changing the compositions of phases, can be seen by comparison of the results listed in Table 4 for selected runs in Au capsules, with the results plotted in Figures 1, 2, and 3. For gabbro with 5% H₂O, the use of Au capsules between 700 and 1000°C produced garnet where none nucleated with Pt capsules; garnet was also present in the 1000°C run using Ag-Pd. A similar difference occurred with tonalite–5% H₂O. With Ag-Pd capsules, garnet formed only at 850°C and above, whereas in Au, it occurred down to 700°C, the lowest-temperature run. No quartz occurred in the 700°C run with Au, whereas with Ag-Pd capsules it should be present. No kyanite occurred in runs with Au, whereas it was present up to 925°C in Ag-Pd capsules.

Run	Temperature °C	H ₂ 0 added wt %	Time hours	Results
226	600	27	9	Oz, Ab, Or, Ms, Ga
227	610	29	9	Qz, Ab, Or(tr), Ms, Ga, L
359	635	12	20	Qz, Ab, Ms, Co(?), Ga(tr), L
270	635	38	16	Qz, Ab, Ms, Ga(tr), L
357	660	9	22	Qz, Ab, Ms, L
353	660	12	23	Qz, Ms, L
271	660	35	16	Qz, Ms, L
374	700	1	23	Qz, Ab, Or, Ms, Ga, L
307	700	5	41	Qz, Ab, Ms, Ga, L
310	700	10	27	Qz, Ms, L
240	825	36.3	6	A
•	700	36.3	10	QZ, MS, L
231	725	32	20	QZ, MS, L
242	825	37.3	10	On Maltri I
202	725	15	20	Q_2 , Ms(C1), U
202	750	22	20	Q_Z , Ms, Co(tr), D
386	750	24	12	Oz Me Co. L
301	750	25	22	Ω_z , Ms(tr), Co. L
229	750	40	24	Ky(tr), Co. L
395	750	43	12	Ky(tr), Co, L
293	775	15	22	Oz, Co, L
337	775	20	22	Oz(tr), Co, L
325	775	23	27	Ky, Co, L
219	775	46	21	Ky(tr), Co, L
303	795	5	20	Qz, Ab, Ms, Co, L
257	800	0	23	Qz, Ab, Or, Ms, Ga
283	800	15	20	Qz, Co(tr), L
223	800	32	21	Co(tr), L
302	820	5	20	QZ, AD, MS(?), CO, L
306	820	9	22	Qz, CO, L Qz Ab Qr $Mc(tr)$ $Co(tr)$ Co $I(tr)$
230	023	45	13	(22, RD, OI, RE(U), CO(CI), Ga, D(CI))
202	825	15	23	OZ. Co. L
388	850	3.2	18	Oz. Ab. Co. Ga(?). L
280	850	14	20	Co, L
230	875	0	25	Qz, Fsp, Co, Ga, L
390	875	2.7	10.5	Qz, Fsp, Co, Ga, L
382	875	5	10	Qz, Co, L
289	940	9.5	9	
+	875	9.5	11	Qz, Co, L
288	900	9.5	11	Qz, Co, L
279	900	15	20	Co, L
284	925	9.5	9	Si(?), Co, L
354	950	5	23	Qz, S1(?), Co(tr), L
241	1000	0	3	Qz, Fsp, Co, Ga, L
269	1000	0	43	Qz, Fsp, Co, L
363	1000	5	5	Qz, Co, L
266	1050	D	42	(2z, Fsp, ky(tr), co, L)
265	1100	0	4/	QZ, KY(?), CO(CI), L
501	1125	1.0	23	
262	1200	1.0	37	Oz. Si. L
203	1315	0	5	X=1 011 D
270	1200	0	5	Co(tr?), L
247	1250	õ	5	Oz(tr)
254	1315	0	5	
	1240	0	5	Si(tr), Co(tr), L
249	1300	0	5	Co(tr), L

 Table 4. Results of quenching experiments for muscovite granite (L26) at 15-kbar pressure

Table 5. Selected runs for microanalyses at 15-kbar pressure and 5% H₂O

Temp.	Time	Capsule	Run No.	Result
X.			Gabbro	DW-1
1000°C	5 h	Au	493	Ga + Cpx + Hb + L
950°C	15 h	Au	494	Ga + Cpx + Hb + L
900°C	36 h	Au	489	Ga + Cpx + Hb + L
800°C	3 days	Au	490	Ga + Cpx + Hb + L
700°C	53.5 h	Au	492	Ga + Cpx + Hb + L
			Tonali	te 101
1025°C	3 h	AgaoPd70	435	Ga + Cpx + L
1025°C	3 h	Ag75Pd25	445	Ga + Cpx + L
975°C	7 h	Ag30Pd70	412	Ga + Cpx + Hb(?) + L
950°C	7 h	Au	609	Ga + Cpx + L
925°C	3 h	Ag30Pd70	441	Ga + Hb + Cpx + Pl + Ky(tr) + L
900°C	5 h	Au	606	Ga + Hb + Cpx + Pl + L
875°C	9 h	AgaoPd70	442	Ga + Hb + Cpx + Pl + Ky(?) + L
850°C	9 h	Ag30Pd70	419	Ga(tr) + Hb + Cpx + Pl + Bio(?) + Ky + L
800°C	15 h	Ag30Pd70	444	Hb + Cpx + Pl + Bio + Ky + L
800°C	30 h	Au	602	Ga + Hb + Cpx + Pl + Bio + L
700°C	40 h	Au	603	Ga + Hb + Cpx + Pl + Bio + L
700°C	63 h	Au	610	Ga + Hb + Cpx + Pl + Bio + L
			Granit	e L26
1000°C	9 h	Au	506	Qz + Co + L
950°C	7 h	Au	509	Qz + Co + L
900°C	25 h	Au	505	Qz + Co + L
800°C	48 h	Au	507	Ms + Pl + Qz + Co + L
700°C	90 h	Au	508	Ms + Pl + Qz + Ga + L
650°C	5 days + 21 h	Au	510	Ms + Pl + Qz + Ga + L

at different rates. Therefore, these analyses were discarded.

Runs using Au capsules with 5% H₂O added are listed in Table 5 for gabbro, tonalite, and granite compositions at temperatures of 650, 700, 800, 900, 950, 1000, and 1025°C. The phase results are broadly consistent with those shown in Figures 1, 2, and 3, with the differences described in the preceding section. Electron-microprobe analyses were performed for 10 elements (Si, Ti, Al, Cr, Fe, Mn, Mg, Ca, Na, and K) for garnet, clinopyroxene, amphibole, plagioclase, muscovite, and glass. For most runs, there is considerable scatter of analyses from one mineral grain to another, with less variation from center to margin of individual grains. Ranges of values and average compositions are plotted in Figures 6 through 10. Glass compositions plotted are averages of 4 to 10 analyses. We have eight tables of analyses that, unfortunately, cannot be fitted into this paper. Space limitations also preclude detailed comparison of our analyses with related results by Green and Ringwood (1972), Allen and Boettcher (1978, 1983), Allen et al. (1975), and Stern and Wyllie (1978).

Garnet

Garnet analyses are plotted in Figure 6A. Note the range of results at each temperature. Garnet synthesized at 950°C contains less grossular component in the center than in the margin. Garnet synthesized at 800°C exhibits less zoning. The average values in Figure 6B define a trend showing significant decrease in pyrope component with decreasing temperatures for both gabbro and tonalite. There is also a decrease of grossular components in garnet as rock composition becomes more silicic from gabbro to tonalite to rhyodacite. Data for rhyodacite with 5% H₂O at 13.5 kbar were reported by Green and Ringwood (1972), with garnet compositions located on the upper right-hand side of the tonalite curve in Figure 6B.

Abbreviations: Qz = quartz; Ab = albite; Or = orthoclase; Ms = muscovite; Ga = garnet; Fsp = alkali-feldspar solid solution; Co = corundum; Ky = kyanite; Si = sillimanite.

Amphibole-out occurred between 900 and 950°C in Au capsules, whereas a trace of amphibole may remain in the 975°C run with an Ag-Pd capsule. In the granite-water system, results in Au capsules between 650 and 1000°C were the same as those in Pt capsules, probably because of the smaller Fe content of the granite.

ANALYTICAL RESULTS FROM GOLD CAPSULE RUNS

Several runs made in Pt and Ag-Pd capsules were originally selected for microprobe analyses. Figure 5A shows the percentage of iron loss (for glass) quenched from above the liquidus as a function of time. Figure 5B shows the difference in Mg/(Mg + Σ Fe) values for coexisting garnet, clinopyroxene, and glass using Ag₃₀Pd₇₀ and Ag₇₅Pd₂₅ capsules under the same conditions. Different phases lose iron



Fig. 4. Phase relations of the calc-alkaline rock series as a function of SiO_2 at 15 kbar and with 5% H₂O. Rectangles indicate the temperatures of phase boundaries from Figures 1, 2, and 3. The vapor-out boundary is situated a few degrees above the solidus. For abbreviations, see Tables 2, 3, and 4.



Fig. 5. Absorption of iron by $Ag_{30}Pd_{70}$ and $Ag_{75}Pd_{25}$ capsules. (A) Percentage of iron loss in glass quenched from liquid of tonalite composition as function of time. (B) Comparison of Mg/(Mg + Fe) values for coexisting garnet, clinopyroxene, and glass quenched from two runs differing only in capsules, $Ag_{30}Pd_{70}$ and $Ag_{75}Pd_{25}$.



Fig. 6. Garnet compositions from gabbro and tonalite, partially melted at 15 kbar in Au capsules, with 5% H_2O added. (A) Range of analyses in each sample. (B) Trend lines as a function of temperature shown by average analyses.

Clinopyroxene and amphibole

Clinopyroxene compositions for each run with gabbro are plotted in Figure 7. There is considerable overlap of results from 700 to 1000°C. The average compositions for each temperature are closely clustered, with no defined variation as a function of temperature. The average composition of clinopyroxene in tonalite at 1025°C has a somewhat lower Mg/(Mg + Σ Fe) value than that in gabbro.

Average amphibole analyses for gabbro and tonalite, plotted in Figure 7, are very similar. According to the classification of Leake (1978), the amphiboles lie close to the boundary between magnesio-hornblende and tschermakitic hornblende.



Fig. 8. Plagioclase compositions from partly melted tonalite and granite with 5% H_2O at 15 kbar. (A) Individual analyses from runs in Au capsules. (B) Average analyses from tonalite as a function of temperature, compared with the zoned plagioclase in original tonalite. Results of Piwinskii (1968) on the same rock at 2 kbar with excess H_2O are shown for comparison.

Plagioclase and muscovite

Plagioclase analyses for granite and tonalite runs are plotted in Figure 8A. Results for granite at 650 and 700°C remain similar to the 5% An in the original plagioclase



Fig. 7. Clinopyroxene and amphibole compositions in partly melted gabbro and tonalite in Au capsules, with 5% H_2O at 15 kbar. The closed symbols indicate the composition of amphibole in gabbro.



Fig. 9. Compositions of glass and crystals quenched from partially melted tonalite at 15 kbar with 5% H_2O added. All runs were in Au capsules, except for the open circles for glasses from Ag-Pd capsules. The dashed lines show the average calc-alkaline rock trend.

(Huang and Wyllie, 1973). For the tonalite, the average plagioclase compositions (close to clustered analyses despite broad ranges) show increase of An between 900 and 800°C, and decrease of An between 800 and 700°C (Fig. 8B). This is probably related to changes resulting from proximity to the albite-jadeite reaction and the retrograde curvature of plagioclase-out in Figure 2. Piwinskii (1968) determined the composition of plagioclase in the same tonalite at 2 kbar with excess water and found the expected increase of An content with increasing temperature, as shown in Figure 8B. There is a decrease of 1-2% An component in plagioclase from tonalite run in Ag-Pd capsules, compared with Au capsules.

Muscovite was analyzed in two granite runs. The paragonite components at 700 and 650°C were, respectively 5.9 and 3.7 mol%, in contrast to 6.7 mol% paragonite in muscovite of the original granite (Huang and Wyllie, 1973).

Glass in tonalite

The composition of glasses quenched from the melting interval for the tonalite were measured at 950, 900, and 800°C, with results compared with mineral analyses in the AMF and CMS diagrams of Figure 9. The glasses at 800–900°C contain 71.6–72% SiO₂, 3.2-4.2% Na₂O, and 2.8-3.1% K₂O (cf. Table 1). The runs in Au capsules follow the calc-alkaline composition trend quite well in the AMF diagram, but deviate somewhat from this trend in the CMS diagram. The loss of iron from samples run in Ag-Pd capsules is obvious in Figure 9A.

If the difference between the total of each analysis and 100% is equated to the dissolved H_2O in the glasses, and thus to that dissolved in the original H_2O -undersaturated liquid, the results indicate 12–15% H_2O between 800 and 950°C, compared with an estimated saturation value at 15 kbar of 19% (poorly constrained in Fig. 2).



Fig. 10. Compositions of glass and crystals quenched from partially melted granite in Au capsules at 15 kbar with 5% H_2O added. The dashed lines show the average calc-alkaline rock trend.



Fig. 11. Compositions of crystals coexisting with liquid in partially melted gabbro in Au capsules with 5% H_2O at 15 kbar. Garnet compositions at 1000 and 700°C are extrapolated from data measured at other temperatures (Fig. 6). The dashed lines show the average calc-alkaline rock trend.

Glass in granite

The compositions of glasses quenched from the melting interval for the granite were measured at six temperatures. The analyses were published by Huang and Wyllie (1981), and results are plotted in Figure 10. The glass compositions change fairly regularly with increasing temperature (although the 800°C glass departs from the main trend). At 650 and 700°C, SiO₂ is in the range 61.4-65.5%, Al₂O₃ in the range 22.6-26.7% (considerably higher than in the original granite; Table 1), K₂O is about twice as high as

in the original granite, and Na₂O is somewhat lower. The glass composition has similarities with syenite. Between 700 and 900°C, SiO₂ increases to the 75% level, and Al₂O₃ and K₂O reach granitic levels. The Na₂O content increases to the granitic level between 800 and 900°C, where the plagioclase dissolves. If the difference between the total analyses and 100% is equated to the H₂O content of the glasses, and thus to that of the original H₂O-undersaturated liquids, the results indicate that dissolved H₂O changed from about 11–13% between 650 and 800°C, with



Fig. 12. The dashed lines show the average calc-alkaline rock trend. (A) If liquids are assumed to lie on the dashed trend line, the bulk mineral composition must be as shown. (B) From partial modal analyses of partially melted gabbro in Au capsules at 15 kbar with 5% added H_2O , the analyzed minerals from Figure 11 yield by calculation the bulk mineral compositions plotted as a function of temperature. The plotted liquid compositions in equilibrium with these calculated mineral assemblages diverge significantly from the calc-alkaline trend.

Fig. 13. Variation of Mg/(Mg + Fe) for coexisting liquids and crystals in Au capsules at 15 kbar with 5% H_2O . The dashed lines and solid lines represent results for gabbro and tonalite, respectively. Arrows show Mg/Mg + Fe) for the rock compositions.

a decrease to about 7–8% associated with the increased melting where plagioclase and muscovite disappear between 800 and 900°C. According to Figure 3, about 22% H_2O is required for saturation of the liquid at 15 kbkar.

Liquid in gabbro

The presence of quench crystals precluded reliable measurement of liquid composition for the gabbro. However, a mass-balance calculation was made to determine if the liquid compositions were close to the average calc-alkaline-rock trend line. The compositions of average garnets, clinopyroxenes, and amphiboles transferred from Figures 6 and 7 to Figure 11 were used in the calculations. The first assumption is that the liquid compositions follow the calc-alkaline trend in terms of the (Na₂O + K₂O)–MgO– FeO, as illustrated in Figure 12A; then, a series of calculations were made to determine whether the same liquids would also follow the trend in terms of CaO–(MgO + FeO)–SiO₂ in Figure 12B.

The percentages of liquid produced through the melting interval were point counted petrographically from the run products. The results are 25, 40, 52, 60, and 80% by volume with 5% uncertainty, respectively, at 700, 800, 900, 950, and 1000°C. The percentages of garnet, clinopyroxene, and amphiboles could only be roughly estimated from the polished sections. The percentages of the minerals in Figure 11 required to keep the liquids on the calc-alkaline trend in Figure 12A, were calculated. The bulk crystal composition required to yield the liquids following the trend is indicated by the open circle in Figure 12A; the shaded area indicates the limited range of the bulk crystal composition when the maximum variation of the trend is taken into account, giving the range between the pair of arrows. The bulk crystal composition was then

Fig. 14. Variation of Na/K for coexisting liquids and crystals in Au capsules at 15 kbar with 5% H_2O . The dashed and solid lines represent results for gabbro and tonalite, respectively. Arrows show log(Na/K) for the rock compositions.

used to calculate the average modal percentage of crystals through the melting interval. Finally, these modal percentages of the crystals and their compositions (Fig. 11) were used to calculate the liquid compositions plotted in Figure 12B. The results diverge from the calc-alkaline trend in Figure 12B. The maximum liquid variation that could be produced from the calculated mineral assemblages lies between the pair of arrows. Similarly, if it was assumed that the liquids lay on the calc-alkaline trend line in Figure 12B, the corresponding calculation showed that the liquids could not lie on the trend in Figure 12A. Thus, although the liquid compositions are not known, it is demonstrated that the liquid path does not follow the calcalkaline trend.

DISTRIBUTION OF ELEMENTS AS FUNCTION OF TEMPERATURE

Two chemical parameters of significance in magmatic history are the Mg-number, represented in Figure 13 as the atomic ratio Mg/(Mg + Fe), and Na/K, represented in Figure 14 as the log of the atomic ratio. Figures 13 and 14 compare the values of these parameters for the bulk rock compositions of gabbro and tonalite with the values derived from the analyses of minerals and glasses (plotted in Figs. 6, 7, 8, and 9) through the melting intervals of gabbro and tonalite.

The Mg-numbers of garnet (Fig. 13) are lower than those of coexisting amphibole, clinopyroxene, and liquid, but at high temperatures they are similar to or slightly lower than those of the rocks; they decrease rapidly with decreasing temperature in both gabbro and tonalite. The variation of Mg-numbers of clinopyroxene with temperature is small, but the Mg-numbers are much higher than the coexisting garnet and amphibole, and higher than those of the rocks.







Fig. 15. The partition coefficients of Mg/Fe between coexisting minerals and glass as a function of temperature with 5% H_2O at 15 kbar. The dashed and solid lines are for gabbro and tonalite compositions, respectively. The dotted and dash-double dot lines give K_D values between clinopyroxene and garnet in anhydrous tholeiite at 15 kbar, interpolated from Raheim and Green (1974) and Ellis and Green (1979). The dash-dot line gives K_D values between glass and garnet from a pelite composition (Green, 1977).

The compositions of amphibole in both gabbro and tonalite are similar in terms of Mg-number, which is close to the value for the gabbro, but higher than that for the tonalite (Fig. 13). Figures 13 and 14 also show that amphibole variations in Mg-number and Na/K with temperature are small. The Mg-number of the amphibole appears to be nearly independent of bulk composition, as well as temperature. Na/K ratio, on the contrary, is significantly controlled by bulk composition. The Na/K for amphibole in tonalite is slightly lower than that of the tonalite, whereas amphibole in gabbro changes from slightly lower to slightly higher than that of the gabbro between 800 and 700°C. The Na/K ratio of plagioclase in gabbro, considerably higher than that in tonalite, shows little variation with temperature.

The Mg-numbers of successive liquids are lower than the coexisting amphiboles but higher than the coexisting garnet. The Na/K ratio of liquids increases slightly with degree of partial melting.

Partition coefficients among coexisting phases

Figure 15 shows the partition coefficients of Mg/Fe ratio as a function of temperature for gabbro and tonalite compositions. For gabbro, the partition coefficients of Mg/Fe between coexisting clinopyroxene and garnet, $K_D = (Mg/Fe)_{cpx}/(Mg/Fe)_{Ga}$, and between clinopyroxene and amphibole decrease with increasing temperature. For tonalite, the K_D values between amphibole and garnet, amphibole and glass, and glass and garnet decrease with increasing temperature.

Raheim and Green (1974) experimentally determined the temperature and pressure dependence of the Fe-Mg



Fig. 16. The partition coefficients of Na/K and Ca/Na between coexisting minerals and glass as a function of temperature with 5% H_2O at 15 kbar. The dashed and solid lines are for gabbro and tonalite, respectively.

partition coefficient $(K_{\rm D})$ for coexisting garnet and clinopyroxene. Our results on basaltic composition for $K_{\rm D}$ vs. temperature are in good agreement with theirs, as shown in Figure 15. Note that the definition of $K_{\rm D}$ used in our study, (Mg/Fe)_{cox}/(Mg/Fe)_{Ga}, is different from theirs, (Fe/ Mg)_{Ga}/(Fe/Mg)_{cpx}, but the actual $K_{\rm D}$ value is the same. Ellis and Green (1979) redetermined the coefficient by taking the effect of Ca on the garnet-clinopyroxene Fe-Mg equilibrium into consideration. They derived a new empirical equation by incorporating the effect of the Ca component in garnet. When the equation was applied to calculate $K_{\rm D}$ by using the Ca component in garnets at 800, 900, and 950°C from our experiments, the K_D values are significantly higher than our experimentally determined data. This suggests that some other parameter that was not identified by Ellis and Green (1979) may significantly affect the $K_{\rm D}$ value. These unknown parameters cause the inconsistency between our data and results calculated from Ellis and Green (1979). However, we are unable to explain why our data are consistent with those of Raheim and Green (1974).

The partition coefficients of Mg/Fe between hydrous glass and garnet of a model pelite composition at 15 kbar (Green, 1977) also show close agreement with our tonalite data, in spite of different bulk composition. However, the same coefficient for Mt. Hood andesite determined by Allen and Boettcher (1983) at 900°C and 19 kbar is significantly lower (0.8) than ours (1.4 at 900C° and 15 kbar).

Figure 16 shows the partition coefficients of Na/K and Ca/Na ratios as a function of temperature. The different partitioning of Na/K and Ca/Na between coexisting plagioclase and liquid is evident. The Na/K ratio in plagioclase is much higher than that in glass, but the Ca/Na ratio is lower in plagioclase than in glass. The K_D of Na/K between plagioclase and glass and that of Ca/Na between glass and plagioclase decrease with increasing temperature. In contrast to plagioclase, amphibole in tonalite has lower Na/K and higher Ca/Na than the coexisting liquid. The $K_{\rm D}$ of Na/K between amphibole and glass decreases with increasing temperature whereas the $K_{\rm D}$ of Ca/Na between amphibole and glass increases with increasing temperature.

PETROLOGICAL APPLICATIONS

The generation of magmas by differentiation of a parent or by partial fusion is complex and probably intermediate between equilibrium and fractional conditions. However, equilibrium experimental results are required as a starting point. Our experimentally determined phase diagrams, although not representing perfect equilibrium, nevertheless define the phase relationships well enough to elucidate processes. The results on liquid compositions and the distribution of elements between coexisting crystals and liquids are reliable, having been measured for runs complete in Au capsules. They provide some basis for prediction of the differentiation trends of hydrous basaltic and andesitic magmas in the deep crust or uppermost mantle and for the products of anatexis of deep crustal rocks composed of gabbro, tonalite, and granite or their metamorphic equivalents. A pressure of 15 kbar is attained at a depth of about 55 km in thickened crust of orogenic belts.

Amphibole fractionation at 55-km depth

It has been suggested that amphibole fractionation exerts a major control on the formation and differentiation of the calc-alkaline rock suite (e.g., Boettcher, 1973; Cawthorn and O'Hara, 1976). Figure 13 shows that Mg-numbers of amphibole in gabbro (basalt) and tonalite (andesite) lie in a small range from 56 to 60 and are nearly independent of temperature and bulk composition. The amphiboles have Mg-numbers close to those of basalt, but much higher than those of andesite, as well as of the liquids in the crystallization interval of andesite. These Mg-numbers are in good agreement with the values between 59 and 62 reported by Holloway and Burnham (1972) for amphibole in basalt of similar composition at 5 and 8 kbar.

Ringwood (1974) used the data of Holloway and Burnham (1972) to support his proposal that fractionation of amphibole from basaltic magmas may not cause ironenrichment in differentiating basalt. Our results for gabbro are consistent with this conclusion as illustrated in Figures 11A and 13. However, our data demonstrate in addition that precipitation of amphibole from hydrous andesitic magma at this depth may contribute to iron-enrichment of liquids (Fig. 13). The latter conclusion is contradicted by the data reported by Green (1972) on amphiboles in and esite (Mg-number = 48) with 2% to 10% H₂O between 5 and 15 kbar. He reported Mg-numbers for amphibole lower than those plotted in Figure 13. Allen et al. (1975) and Allen and Boettcher (1978) also reported amphibole analyses from basalts and andesites through pressure ranges including 15 kbar with H₂O-CO₂ mixtures giving variations in $X_{H_{20}}$. Their amphibole analyses covered a wide

compositional range, with overall higher Mg-numbers than ours (Fig. 13), and on this basis they concluded that amphibole fractionation could cause iron-enrichment in magmas. However, this contradiction now appears less pronounced, since the new data of Allen and Boettcher (1983) on the same samples, with less iron loss, gives Mg/ (Mg + Fe) values for amphibole closer to our results in Figure 13.

The variety of amphibole compositions determined in experimental studies, and especially those of Allen and Boettcher (1978, 1983) under a variety of experimental conditions, implies that many factors including pressure, water content, noble-metal capsule, and oxygen fugacity, as well as liquid composition and temperature, may affect amphibole composition. Similarly, many factors will influence amphibole composition in natural magmas. In order to evaluate the actual role of amphibole fractionation during magma differentiation, a detailed and systematic experimental program for determination of amphibole composition as a function of the variables is required.

Magma differentiation at 55-km depth

Although fractionation of amphibole from basaltic magma may be capable of producing differentiated liquids with Mg/Fe corresponding to those of the calc-alkaline trend at least during the early stages of differentiation, our results indicate that it is not the dominant process in hydrous basalts at 55-km depth. Fractionation of clinopyroxene and garnet together is the main process causing changes in composition of hydrous basalt, because these two minerals are the liquidus phases, with subordinate amphibole joining them below the liquidus; these three minerals are coprecipitated through several hundred degrees (Fig. 1). The analyses and calculations plotted in Figures 11 and 12 confirm that the differentiating hydrous basaltic liquid does not follow the calc-alkaline trend. The crystallization of clinopyroxene with high Mg-numbers averaging 70 tends to produce a liquid with high Fe/Mg, but this effect is offset at least at the lower temperatures by the low Mg-numbers of garnet (Fig. 13). Crystallization of amphibole controls Na/K in liquids until the low temperatures where plagioclase begins to crystallize.

Garnet and subordinate clinopyroxene are also the liquidus minerals in crystallization of hydrous andesite (Fig. 2), joined within a small temperature interval by amphibole and plagioclase, with biotite and quartz appearing at lower temperatures. Precipitation of clinopyroxene and amphibole, with Mg-numbers much higher than that of the liquids, tends to cause iron-enrichment of the liquids, but garnet operates in the other direction (Fig. 9), as shown by values of K_D for Hb/glass and glass/Ga in Figure 15. The glass analyses plotted in Figure 9 indicate that liquid compositions in the middle-temperature range approximate the calc-alkaline trend, with slight divergence toward higher CaO/(MgO + FeO) with decreasing temperature. The Na/K is mainly controlled by the relative amount of amphibole and plagioclase precipitating. Because of the very high $K_{\rm D}$ for Pl/glass (Fig. 16), we expect the effect of plagioclase to dominate, causing decrease of Na/K in the liquid with decreasing temperature, which is consistent with the glass analyses in Figure 14.

We do not expect to find granite or rhyolite magma differentiating at a depth of 55 km, but Figures 3 and 10 illustrate the controls on such behavior. Hydrous rhyolite liquid would precipitate quartz alone (excluding the metastable corundum) through 100°C or more, causing depletion of the liquid in SiO₂, as illustrated by the glass compositions plotted in Figure 10B. With subsequent coprecipitation of plagioclase, the depletion of the liquid in SiO₂ continues, with the formation of liquid similar in composition to sygnite (Huang and Wyllie, 1981).

Anatexis of lower crust, thickened to 60 km

It is generally assumed that the base of the continental crust is composed dominantly of the metamorphic equivalents of gabbro and tonalite, hydrated to greater or lesser extent. At compressive plate boundaries with thickened crust, or during the Archean when localized subduction might have been more prevalent, we consider also the prospect that granitic rocks could be carried as deep as 55-60 km. The mineral assemblages for these rocks at 55km depth are given in the subsolidus regions of Figures 1, 2, 3, and, in combination, in Figure 4. Wyllie (1977) reviewed the conditions for anatexis of the same range of rock compositions at 10 kbar, corresponding to crustal thickness of 35-40 km, concluding that H₂O-undersaturated granite or rhyolite magma was the normal product of progressive metamorphism of many crustal rocks at moderate depths and that the generation of magmas less siliceous required the addition of heat or magmatic material or both from the underlying mantle.

The mineralogy in a thickened crust differs from that in the normal crust by the addition of the high-pressure minerals garnet and clinopyroxene in the gabbro and tonalite, but the muscovite granite retains essentially the same mineral assemblage. Wyllie (1977) reviewed the conditions for partial fusion of the rocks both with pore fluid and without. In this paper, we consider only the anatexis of the rocks in the presence of aqueous pore fluid, using compositions of glasses measured in runs with 5% H_2O as a possible guide to liquid paths. Unfortunately, we have no glass compositions for the gabbro, and it was difficult to obtain reliable glass measurements near the solidus with small fractions of melting.

Anatexis of gabbro and tonalite under these conditions involves similar minerals, with a quartz field-boundary controlling the composition of the first liquid. The first liquids developed from either rock are therefore siliceous, and probably similar in composition. Successive liquids, however, will follow different paths because quartz and plagioclase (with biotite) remain among the residual minerals through a wider temperature in the progressive fusion of tonalite than of gabbro. The analyses and calculations based on Figures 11 and 12 indicate that partial fusion of hydrous gabbro at this depth does not yield a series of liquids with chemical variation corresponding to the calc-alkaline rock series. The glass analyses from partially melted tonalite indicate a liquid trend with CaO/ (MgO + FeO) somewhat higher than the calc-alkaline trend. At 900°C, with a generous allowance of 5% H₂O, the residual mineral assemblage Hb + Ga + Cpx + Pl coexists with liquid containing 72% SiO₂, 4.2% Na₂O, and 3.1% K₂O. Despite its high SiO₂ content, this does not correspond to a granite because granite under these conditions would precipitate only quartz through a wide temperature interval below its hydrous liquidus (see Fig. 3). The evidence indicates that if magmas are generated by partial fusion of gabbro and tonalite in thickened continental crust, they do not correspond to the rocks composing the calc-alkaline batholiths, nor do they give rise to the batholiths by fractional crystallization.

The partial melting of deep granite proceeds along a path quite different from that for tonalite and gabbro. The alkali feldspar dissolves first, yielding a potassic liquid, and subsequent fusion is controlled essentially by the quartz-plagioclase boundary. The quartz volume expands considerably at high water pressures, and the liquid compositions coexisting with quartz and feldspar are thus forced to lower SiO₂ contents (Huang and Wyllie, 1975). This is indicated in Figure 10B. The relatively low-SiO₂, high- K_2O liquids at 650 and 700°C have some characteristics of syenite.

Trondhjemite is an important component of Archean igneous activity and of some more recent calc-alkaline batholiths. The data in this paper do not provide evidence for the conditions of generation of trondhjemites, but they do demonstrate some conditions unsuitable for their formation. Na/K ratios as high as 2-4 are characteristic of trondhjemites. None of the hydrous glasses analyzed in the tonalite (Fig. 14) or granite approached this value, and extrapolation from the analyzed glasses through other parts of the determined phase relationships (Figs. 2 and 3) suggest that trondhjemites are not simply related to either granites or tonalites at 15 kbar. We have no analyses of glasses from the gabbro, but within the phase relationships at 15 kbar (Fig. 1), there appears to be a prospect that liquids of appropriate composition might be found at moderate H₂O contents near the plagioclase-out and quartz-out boundaries. Holloway and Burnham (1972) and Helz (1976) analyzed glasses from partially melted hydrous basalts at lower pressures, reporting trondhjemitic to tonalitic compositions with 15-30% melting, 850 to 1000°C.

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REFERENCES

Allen, J.C., and Boettcher, A.L. (1978) Amphiboles in andesite and basalt: II. Stability as a function of *P*-*T*-*f*_{H2O}-*f*_{O2}. American Mineralogist, 63, 1074-1087. (1983) The stability of amphibole in andesite and basalt at high pressures. American Mineralogist, 68, 307–314.

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- Allen, J.C., Boettcher, A.L., and Marland, G. (1975) Amphiboles in andesite and basalt: I. Stability as a function of P-T- f_{O_2} . American Mineralogist, 60, 1069–1085.
- Bateman, P.C., Clark, L., Huber, N.K., Moore, J.G., and Rhinehart, C.D. (1963) The Sierra Nevada batholith, a synthesis of recent work across the central part. U.S. Geological Survey Professional Paper, 414-D, D1–D46.
- Boettcher, A.L. (1973) Volcanism and orogenic belts—The origin of andesites. Tectonophysics, 17, 204–233.
- Boettcher, A.L., and Wyllic, P.J. (1968) The quartz-coesite transition measured in the presence of a silicate liquid and calibration of piston-cylinder apparatus. Contributions to Mineralogy and Petrology, 17, 224–232.
- Boyd, F.R., and England, J.L. (1960) Apparatus for phase-equilibrium measurements at pressures up to 50 kilobars and temperatures up to 1750°C. Journal of Geophysical Research, 65, 741-748.
- Boyd, F.R., Bell, P.M., England, J.L., and Gilbert, M.C. (1967). Pressure measurement in single-stage apparatus. Carnegie Institute of Washington Year Book 65, 410–414.
- Cawthorn, R.G., and O'Hara, M.J. (1976) Amphibole fractionation in calc-alkaline magma genesis. American Journal of Science, 276, 309-329.
- Ellis, D.J., and Green, D.H. (1979) An experimental study of the effect of Ca upon garnet-clinopyroxene Fe-Mg exchange equilibria. Contributions to Mineralogy and Petrology, 71, 13–32.
- Green, T.H. (1972) Crystallization of calc-alkaline andesite under controlled high-pressure hydrous conditions. Contributions to Mineralogy and Petrology, 34, 150–166.
- (1977) Garnet in silicic liquids and its possible use as a *P*-*T* indicator. Contributions to Mineralogy and Petrology, 65, 59–67.

—— (1982) Anatexis of mafic crust and high pressure crystallization of andesite. In R.S. Thorpe, Ed. Andesites: Orogenic andesites and related rocks, 465–487. John Wiley, Chichester.

- Green, T.H., and Ringwood, A.E. (1968) Genesis of the calcalkaline igneous rock suite. Contributions to Mineralogy and Petrology, 18, 105–162.
- Helz, R.T. (1976) Phase relations of basalts in their melting ranges at $P_{\rm H_{20}} = 5$ kb. Pt. II. Melt compositions. Journal of Petrology, 17, 139–193.
- Holloway, J.R. (1973) The system pargasite-H₂O-CO₂: A model for melting of a hydrous mineral with a mixed-volatile fluid. I. Experimental results to 8 kb. Geochimica et Cosmochimica Acta, 37, 651–666.
- Holloway, J.R., and Burnham, C.W. (1972) Melting relations of basalt with equilibrium water pressure less than total pressure. Journal of Petrology, 13, 1–29.
- Huang, W.L., and Wyllie, P.J. (1973) Melting relations of muscovite-granite to 35 kb as a model for fusion of metamorphosed subducted oceanic sediments. Contributions to Mineralogy and Petrology, 42, 1–14.

(1974) Melting relations of muscovite with quartz and sanidine in the K₂O-Al₂O-SiO₂-H₂O system to 30 kilobars and outline of paragonite melting relations. American Journal of Science, 274, 378–395.

----- (1975) Melting reactions in the system $NaAlSi_3O_8$ -KAlSi₃O₈-SiO₂ to 35 kilobars, dry and with excess water. Journal of Geology, 83, 737–748.

(1981) Phase relationships of S-type granite with H_2O to 35 kb: Muscovite granite from Harney Peak, South Dakota. Journal of Geophysical Research, 86, 1015–1029.

- Ito, K., and Kennedy, G.C. (1968) Melting and phase relations in the plant tholeiite-lherzolite-nepheline basanite to 40 kilobars with geological implications. Contributions to Mineralogy and Petrology, 19, 177–211.
- Lambert, I.B., and Wyllie, P.J. (1972) Melting of gabbro (quartz eclogite) with excess water to 35 kilobars, with geological applications. Journal of Geology, 80, 693–708.
- (1974) Melting of tonalite and crystallization of andesite liquid with excess water to 30 kilobars. Journal of Geology, 82, 88–97.
- Leake, B.E. (1978) Nomenclature of amphiboles. Canadian Mineralogist, 16, 501–520.
- Merrill, R.B., and Wyllie, P.J. (1973) Iron absorption by platinum capsules in high pressure rock melting experiments. American Mineralogist, 58, 16–20.
- Nehru, C.E., and Wyllie, P.J. (1975) Compositions of glasses from St. Paul's peridotite partially melted at 20 kilobars. Journal of Geology, 83, 455–471.
- Piwinskii, A.J. (1968) Experimental studies of igneous rock series. Central Sierra Nevada batholith, California. Journal of Geology, 76, 548–570.
- —— (1973a) Experimental studies of granitoids from the central and southern Coast Ranges, California. Tschermaks Mineralogische und Petrographische Mitteilungen, 20, 107–130.
- —— (1973b) Experimental studies of igneous rock series, Central Sierra Nevada batholith, California: Part 2. Neues Jahrbuch für Mineralogie Monatshefte, 6, 193–215.
- (1975) Experimental studies of granitoid rocks near the San Andreas fault zone in the Coast-Transverse Ranges, Mohave Desert, California. Tectonophysics, 25, 217–231.
- Piwinskii, A.J., and Wyllie, P.J. (1968) Experimental studies of igneous rock series: A zoned pluton in the Wallowa batholith, Oregon. Journal of Geology, 76, 205–234.
- (1970) Experimental studies of igneous rock series: Felsic body suite from the Needle Point pluton, Wallowa batholith, Oregon. Journal of Geology, 78, 52–76.
- Raheim, A., and Green, D.H. (1974) Experimental determination of the temperature and pressure dependence of the Fe-Mg partition coefficient for coexisting garnet and clinopyroxene. Contributions to Mineralogy and Petrology, 48, 179–203.
- Ringwood, A.E. (1974) The petrological evolution of island arc systems. Geological Society of London Journal, 130, 183–204.
- Stern, C.R., and Wyllie, P.J. (1973) Melting relations and basaltandesite-rhyolite-H₂O and a pelagic red clay at 30 kilobars. Contributions to Mineralogy and Petrology, 42, 313–323.
- (1975) Effect of iron absorption by noble-metal capsules on phase boundaries in rock-melting experiments at 30 kilobars. American Mineralogist, 60, 681–689.
- (1978) Phase compositions through crystallization intervals in basalt-andesite- H_2O at 30 kb with implications for subduction zone magmas. American Mineralogist, 63, 641–663.
- ——— (1981) Phase relationships of I-type granite with H₂O to 35 kb: The Dinkey Lakes biotite granite from the Sierra Nevada batholith. Journal of Geophysical Research, 86, 10412–10422.
- Wyllie, P.J. (1977) Crustal anatexis: An experimental review. Tectonophysics, 13, 41–71.
- —— (1979) Magmas and volatile components. American Mineralogist, 64, 469–500.
- Yoder, H.S., and Kushiro, I. (1969) Melting of a hydrous phase: Phlogopite. American Journal of Science, 267-A, 558-582.

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