

The system tonalite-H₂O at 15 kbar and the genesis of calc-alkaline magmas

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ABSTRACT

Experimental phase relations and well-characterized mineral and melt compositions have been determined for a Sierra Nevada tonalite (andesite) with 2.5 to 10 wt% H₂O added at 15 kbar and 850 to 1100 °C. All results are from experiments conducted in Au capsules (minimal Fe loss to capsule) at oxygen fugacities measured to be near Ni-NiO. With increasing water content, the liquidus mineral changes from clinopyroxene at <3 wt% H₂O to garnet, followed within 50 °C by clinopyroxene at 3 to 9 wt% H₂O, to hornblende at water contents greater than ~9 wt%. Microprobe analyses of glasses quenched from within the tonalite melting interval show an enrichment in Ca relative to (Mg + Fe), where Fe represents total Fe as Fe²⁺, with increasing SiO₂ instead of the typical calc-alkaline trend of approximately constant Ca/(Mg + Fe) from basalt through rhyolite. The results document the importance of garnet and clinopyroxene in andesitic to dacitic compositions at deep-crustal to uppermost-mantle pressures, and they indicate that it is not possible to directly produce magmas of calc-alkaline composition at 15 kbar and the investigated range of water contents by either (1) partial melting of tonalitic to gabbroic (eclogitic) lower crust or (2) crystal fractionation from melts of andesitic to basaltic composition. Melting or fractionation at lower pressures or with lower water contents may produce calc-alkaline liquids as plagioclase replaces garnet as the major Al-bearing phase. Calc-alkaline rocks showing evidence of garnet-liquid equilibration in their REE patterns must also have undergone lower-pressure fractionation in order to explain their major-element compositions.

INTRODUCTION

Understanding the origins of the great volumes of calc-alkaline basalt, andesite, dacite, rhyolite, and their intrusive equivalents found at mature convergent plate margins requires knowledge of the effects of parameters such as pressure, temperature, and magmatic water content on crystal-liquid equilibria in relevant rock systems. Previous work has elucidated some of the phase-equilibrium and geochemical constraints on the petrogenesis of calc-alkaline magmas, yet many questions remain unanswered, especially with regard to crystallization and differentiation at depths of the deep crust to uppermost mantle. One of the key questions for this tectonic environment involves the fraction of tonalite or andesite derived from mantle sources and the fraction derived from crustal sources. Results for the pressure interval 10–15 kbar are appropriate for processes occurring near the mantle-crust boundary in environments where the continental crust is thickened by orogenesis (e.g., the Andes, western North America). This boundary region is also the depth interval in which plagioclase is replaced by garnet, and the phase relationships of the calc-alkaline magma series therefore change significantly from those dominat-

ed by plagioclase, pyroxene, and hornblende at low pressures (e.g., Grove and Baker, 1984; Grove and Kinzler, 1986; Egger and Burnham, 1973; Rutherford et al., 1985) to the high-pressure assemblages including garnet, pyroxene, and hornblende (e.g., Green and Ringwood, 1968; Green, 1972; Stern and Wyllie, 1978; Sekine and Wyllie, 1982).

In another study, we have conducted experiments with mixtures of peridotite and tonalite at 15 kbar in an effort to determine the phase boundaries that control liquid compositions during processes of assimilation or magma mixing in the mantle-crust boundary region (Carroll and Wyllie, 1989). As part of our studies, we found it desirable to re-examine the system tonalite-H₂O under the same experimental conditions. In this paper, we present new experimental results for the water-undersaturated portion of the tonalite (= andesite)-H₂O system at 15-kbar pressure. The data include well-characterized phase assemblages and mineral and quenched-melt compositions for a natural tonalite with 2.5 to 10 wt% H₂O added at temperatures between 850 and 1100 °C. The results of these experiments help in defining plausible crystallization-differentiation or partial-melting processes involving tonalitic compositions in the deep crust or upper mantle. Two major types of information useful in understanding the origin of some calc-alkaline magmas may be derived from the experimental results. For considering tonalites

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TABLE 1. Experimental starting material

Com- posi- tion	CIPW norm		Mode		
SiO ₂	59.14	Quartz	11.7	Quartz	13.0
TiO ₂	0.79	Orthoclase	12.9	Alkali Feldspar	4.5
Al ₂ O ₃	18.23	Albite	32.2	Plagioclase	59.0
Fe ₂ O ₃	2.32	Anorthite	26.2	Biotite	12.5
FeO	3.62	Diopside	0.9	Hornblende	9.0
FeO*	5.71	Hypersthene	9.4	Opaques	2.0
MnO	0.11	Olivine	—		
MgO	2.50	Magnetite	3.4		
CaO	5.92	Ilmenite	1.5		
Na ₂ O	3.81	Apatite	0.7		
K ₂ O	2.19	Corundum	—		
H ₂ O ⁺	0.82				
H ₂ O ⁻	0.04				
P ₂ O ₅	0.30				
CO ₂	0.01				
Total	99.80				

Note: Compositions are given in weight percent and are taken from Bateman et al. (1963). CIPW norms are given in weight percent.

* Total iron as FeO.

or andesites generated by partial melting of more mafic source materials (e.g., hydrous peridotite, subducted oceanic crust, or basalt underplated at the base of the continental or island arc crust), the high-pressure liquidus minerals of the tonalite give information on the identity and composition of possible phases present in the source materials. Residual-liquid compositions from the partially crystallized tonalite provide constraints on plausible differentiated compositions that may be produced by crystal fractionation from tonalite magma at high pressure.

PREVIOUS WORK

Previous experimental studies on tonalite or andesite bulk compositions with H₂O and H₂O-CO₂ mixtures in the range 10–30 kbar include those of Green and Ringwood (1968), Green (1972), Lambert and Wyllie (1974), Stern et al. (1975), Allen and Boettcher (1978, 1983), Allen et al. (1975), and Huang and Wyllie (1968). Petrological applications and summaries of the experimental data have been presented in reviews by Wyllie (1977, 1979), Gill (1981), and Green (1982).

The tonalite used in this study has been the subject of a series of experiments. Piwinski (1973) used excess H₂O at 1, 2, 3, and 10 kbar. Lambert and Wyllie (1974) reported experiments with excess-H₂O between 10 and 30 kbar from the solidus to about halfway through the melting interval. The latter results were extended through the liquidus by Stern and Wyllie (1973), who, in addition, completed experiments in the vapor-absent region, with construction of the H₂O-undersaturated liquidus surface (Stern et al., 1975) and with microprobe analyses of glass and minerals quenched from 30 kbar (Stern and Wyllie, 1978). The tonalite melting experiments noted above were conducted using mostly Ag₃₀Pd₇₀ capsules and suffered from the experimental problem of Fe loss to the capsules and associated difficulties in demonstrating reversible

equilibrium, as discussed in detail by Stern and Wyllie (1973). When the experiments of Huang and Wyllie (1986) on tonalite-H₂O at 15 kbar were being completed in 1975, AgPd capsules were still in use because the phase diagrams extended to temperatures above the melting of Au. However, Huang and Wyllie (1986) completed in addition a few selected experiments with 5% H₂O in Au capsules specifically for microprobe analyses. They also reported differential losses of Fe as a function of time for different phases in different capsule materials, and they noted some specific differences in the phase assemblages produced in experiments using Au as compared with those using AgPd capsules. We have now redetermined the phase relationships for that part of the H₂O-undersaturated isobar (15 kbar) accessible to the use of Au capsules. Some results on tonalite with 5 or 10 wt% H₂O added have been presented as part of a study of the phase-equilibrium controls on reaction between hydrous andesitic magma and ultramafic rock (Carroll and Wyllie, 1989). In this paper, we combine those data with results on tonalite with 2.5 wt% H₂O added and evaluate the effects of crystallization differentiation or partial melting in magmatic processes at pressures near 15 kbar and in the stability field of garnet.

EXPERIMENTAL METHODS

Starting material

A sample of tonalite from the Sierra Nevada batholith, kindly provided by P. C. Bateman and F. C. Dodge, was used in all experiments (tonalite 101, or M127 in Piwinski, 1973). Field and petrographic data for the tonalite are in Bateman et al. (1963). The chemical composition and normative and modal mineral contents of the tonalite are in Table 1. The tonalite was initially ground to pass 200 mesh, then finely ground in an agate mortar to produce a mean grain size of ~10 μm, with rare grains of hornblende or biotite up to ~50 μm in maximum dimension. The powdered starting material was dried at 120 °C and then stored in a desiccator when not being used.

Apparatus and procedures

Experiments were performed in a single-stage piston-cylinder press using a 1.27-cm-diameter piston and a chamber with a hardened steel liner (Boyd and England, 1960). Temperature and pressure calibrations were checked against the reaction albite = jadeite + quartz (Boettcher and Wyllie, 1968). All experiments were conducted using a graphite furnace assembly with NaCl as the confining medium. Reported pressures incorporate no friction correction and are believed accurate to ±5% of the quoted value. A W-Re thermocouple located less than 1 mm above the sample capsule was used to both measure and control experimental temperatures; accuracy and precision are estimated to be ±15 and ±5 °C, respectively. The oxidation state of the sample during the experiments was close to Ni-NiO. An experiment with a

mixture of synthetic magnetite solid solution + ilmenite solid solution + H₂O yielded coexisting Fe-Ti oxide compositions that indicate an oxygen fugacity $\sim 0.5 \log f_{\text{O}_2}$ units above the Ni-NiO equilibrium at 15 kbar (Spencer and Lindsley, 1981). Analysis of coexisting Fe-Ti oxides from a vapor-undersaturated experiment on a syenite at 15 kbar, with the use of the same sample assembly, yields a similar f_{O_2} estimate (Wolf and Wyllie, unpublished data).

Experiments were conducted in Au capsules of 2.5 mm outside diameter that contained 10 to 15 mg of finely ground and dried rock powder. Appropriate amounts of triply distilled water were added with a microliter syringe, and the capsule was arc-welded shut. Monitoring the capsule weight during this process provided a check on water loss during welding. The sealed capsule was embedded in the top several millimeters of an NaCl pedestal that served to position the sample in the middle of the furnace assembly. Experiments were of the synthesis type in which the sample was pressurized to 2 kbar below the desired pressure and then heated to the desired temperature; pressure rose during heating, and the final pressure was obtained by bleeding off excess pressure once the desired temperature had been reached. Quenching was accomplished by turning off the power, resulting in quench rates of approximately 200 °C/s and yielding clear glasses free of quench crystals in all but the most water-rich, near-liquidus experiments. Most experiments were conducted under vapor-absent conditions and produced bubble-free glasses. After quenching, the experimental charges were removed from the salt confining medium, soaked in water to remove any adhering NaCl, and then weighed to check that they had remained sealed.

Choice of experiment duration was guided partly by previous experience and partly by the results of several exploratory experiments at identical conditions but of varying duration. Equilibrium cannot be proven for every experiment because they were not reversed, but all of those reported in this study were of sufficient duration to produce compositionally homogeneous glasses coexisting with euhedral to subhedral crystals of uniform or only slightly varied composition. The only exception was in the case of hornblende crystals that sometimes had cores of clinopyroxene or clinopyroxene-hornblende intergrowths. The rims of hornblende with clinopyroxene cores were very similar in composition to smaller, euhedral hornblende crystals lacking clinopyroxene cores, and we believe they represent equilibrium compositions. Stern and Wyllie (1973) reviewed the problems of completing satisfactory reversals in multiphase rock systems, and Huang and Wyllie (1986) presented a detailed discussion of the matter for this rock under similar conditions.

Charges from successful experiments were sliced vertically using a diamond saw, and one half of the charge was used to prepare a polished thin section for petrographic study and electron-microprobe analysis. Phases identified in the experiments include garnet (Ga), clinopyroxene (Cpx), hornblende (Hb), titaniferous magnetite (Ox), plagioclase (Pl), quartz (Qz), rutile (Rut), biotite (Bi),

TABLE 2. Microprobe analyses of near-liquidus glasses compared with starting composition

	(a)	(b)	(c)	(d)
SiO ₂	59.7	60.0	60.9	61.3
TiO ₂	0.8	0.8	0.8	0.8
Al ₂ O ₃	18.4	18.5	18.0	18.3
FeO*	5.8	5.9	5.5	4.6
MnO	0.1	0.1	0.1	0.1
MgO	2.5	2.3	2.4	2.4
CaO	6.0	6.1	5.9	6.0
Na ₂ O	3.8	3.8	4.0	4.0
K ₂ O	2.2	2.2	2.2	2.1

Note: All analyses recalculated on a water-free basis. Columns are (a) Composition of tonalite 101 starting material. (b) Glass from experiment 41 at 1000 °C, 10% H₂O added. (c) Glass from experiment 29 at 1040 °C, 5% H₂O added. Small amount of garnet present. (d) Glass from experiment 92 at 1100 °C, 2.5% H₂O added. Contains small amount of garnet, often with Fe-Ti oxides in cores.

and glass (Gl, quenched melt). Trace amounts of apatite, zircon, and titanite occur in some of the lower-temperature experiments. Crystal settling was observed in experiments near the liquidus and in those with up to approximately 25% crystals. These charges consisted of a crystal-rich lower portion and an overlying region of crystal-free (or almost so) glass.

Electron-microprobe analyses of experimental products were obtained using either a JEOL electron microprobe at Caltech or a CAMECA electron microprobe at Brown University. Analyses of the same samples with each instrument produced identical results. Both instruments were operated at an accelerating voltage of 15 keV. A 5-nA beam current and a 20- to 30- μ m beam spot were used for analyses of glasses and a 15- to 20-nA current and a 2- μ m spot were used for analyses of crystalline phases. For all glass analyses, Na, K, Si, and Al were measured first to reduce the problems associated with alkali migration under the electron beam. The success of these precautions is demonstrated by the agreement between analyses of superliquidus glasses and the composition of the starting material (Table 2).

EXPERIMENTAL RESULTS

The 15-kbar phase diagram for tonalite-H₂O from Huang and Wyllie (1986) is reproduced in Figure 1. All of the plotted experiments were conducted in Ag₃₀Pd₇₀ (round symbols) or Pt capsules (square symbols). Not plotted are the four additional experiments with 5 wt% H₂O in Au capsules that were completed at 950, 900, 800, and 700 °C for mineral and glass analyses. Figure 1 is a reconnaissance diagram, both because of the limited number of brackets in the vapor-absent region and because of problems associated with use of Ag₃₀Pd₇₀ capsules as reported by Stern and Wyllie (1973) and Huang and Wyllie (1986); these included the failure of garnet to nucleate in Ag₃₀Pd₇₀ under conditions where it is known to nucleate in Au capsules. Results presented herein suggest that loss of Fe from tonalite to the Ag₃₀Pd₇₀ capsules would move the bulk composition into the clinopyroxene

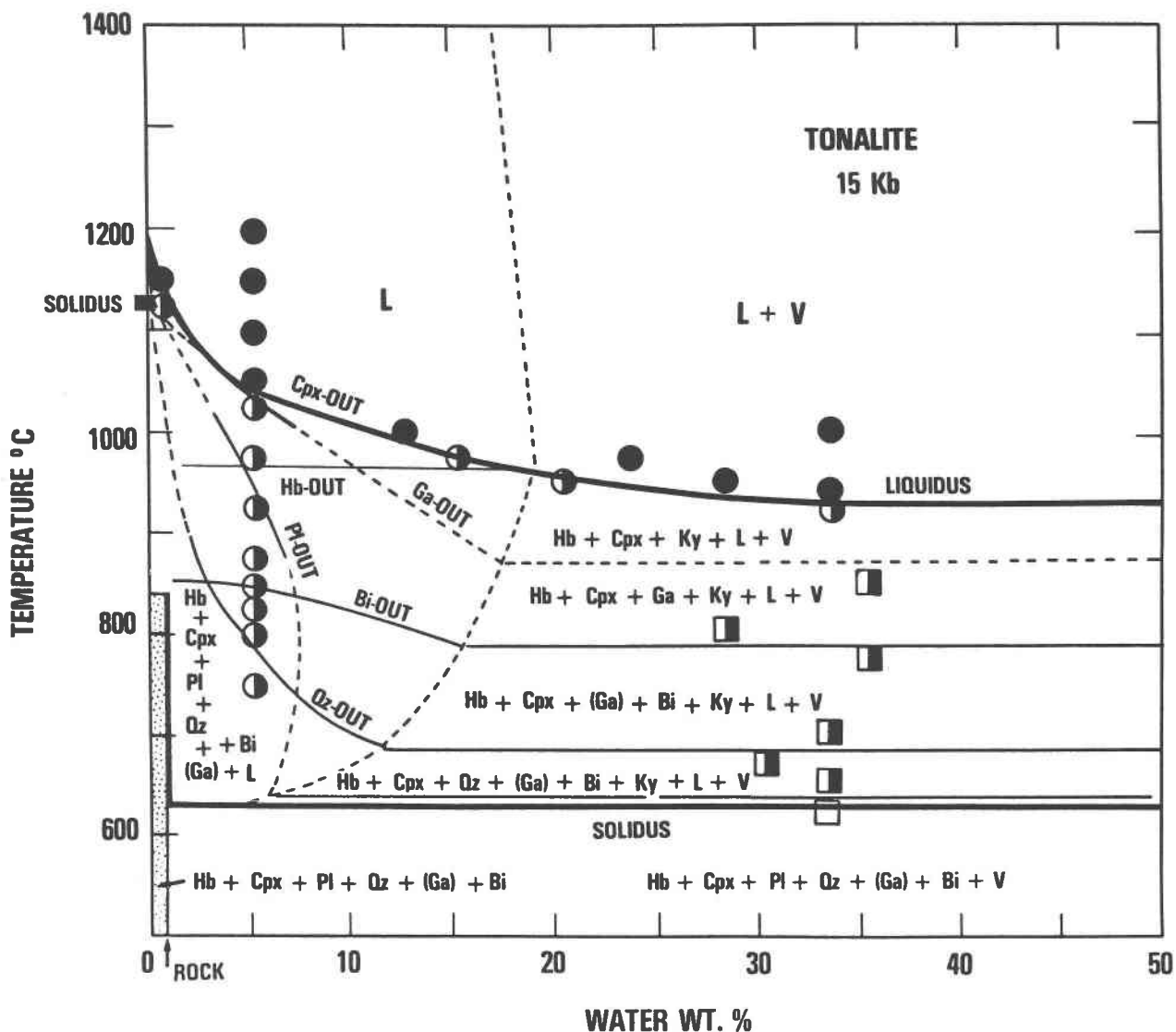


Fig. 1. Isobaric T - $X_{\text{H}_2\text{O}}$ phase diagram for tonalite 101 at 15 kbar, taken from Huang and Wyllie (1986). Square symbols show experiments completed by Lambert and Wyllie (1974). Abbreviations for minerals include Cpx = clinopyroxene, Ga = garnet, Hb = hornblende, Pl = plagioclase feldspar, Bi = biotite, Qz = quartz, Ky = kyanite, L = liquid (melt), V = vapor. Fields with (Ga) should have stable garnet, but it failed to nucleate in experiments performed in $\text{Ag}_{30}\text{Pd}_{70}$ capsules. Duplicate experiments in Au capsules produced garnet-bearing assemblages where expected.

liquidus field, thus explaining the lack of liquidus garnet in the previous study. Our new experiments in Au capsules supplement the previous results with 5% H_2O and concentrate on the phase boundaries in the vapor-absent region up to the temperature limit permitted by Au. These results of limited range may be compared with the reconnaissance diagram in Figure 1.

Phase relations

Experimental conditions and resulting phase assemblages are summarized in Table 3, along with the results of two experiments in Au capsules tabulated by Huang and Wyllie (1986). The results are plotted in isobaric sec-

tions in Figure 2. Water contents given in Table 3 refer to added water, and experimental points in Figure 2 show an additional 0.8 wt% H_2O corresponding to the H_2O bound in biotite and hornblende in the starting material (Table 1). For simplicity, reference to the experiments will cite nominal water added (2.5, 5, or 10 wt%), rather than total H_2O in the charge. Traces of the accessory minerals rutile, titanite, and apatite are noted in Table 3, but they are not represented in Figure 2.

The experiments conducted for this study and resulting phase assemblages are shown in T - $X_{\text{H}_2\text{O}}$ section in Figure 2a. Several experiments were repeated for different durations, and the results for the longer experiments were

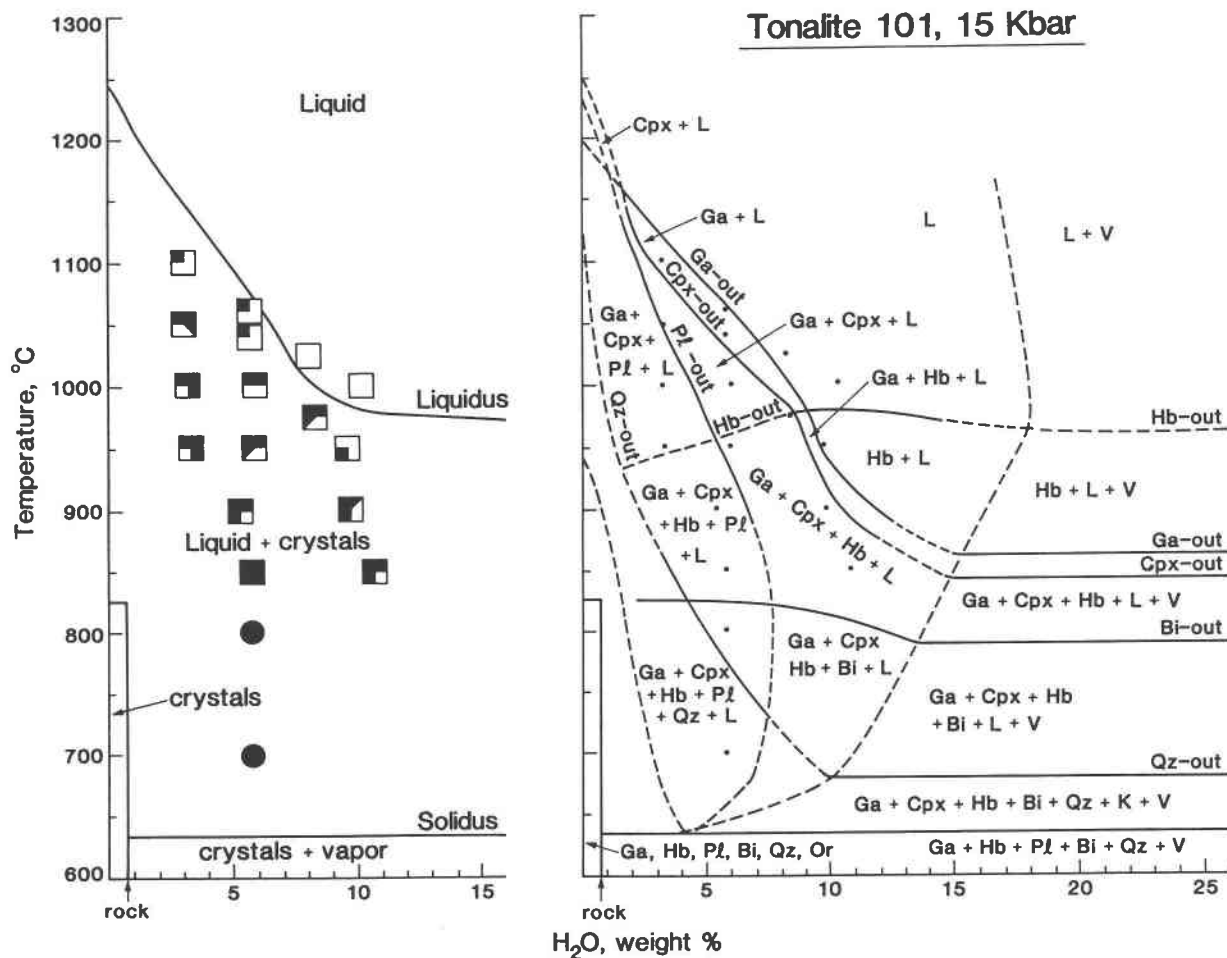


Fig. 2. Isobaric $T-X_{(H_2O)}$ phase diagram for tonalite 101 at 15 kbar, showing (a, left) new experiments conducted in this study using Au capsules, and (b, right) the best estimate of phase relations based on the new vapor-absent results with Au capsules and the previous results shown in Fig. 1. Half-filled quadrants of symbols in (a) indicate uncertainty about stability of the indicated phase (Ga—upper left; Cpx—upper right; Hb—lower left; Pl—lower right).

adopted if different phase assemblages were observed. As expected, reactions became more sluggish with less H₂O and at lower temperatures. With 2.5% H₂O at 1000 °C, plagioclase and quartz remained after 24 h, and there was a trace of poorly formed clinopyroxene; after 60 h, clinopyroxene was well-formed and slightly more abundant, plagioclase was reduced to trace amounts, and a few amoeboid-shaped grains of quartz remained. With 5% H₂O at 950 °C, experiments of 7 and 16.5 h were sufficient to melt all plagioclase and hornblende in the starting material and to grow well-formed garnet and clinopyroxene. At 900 °C with 5% H₂O, however, plagioclase remained after 5 h but disappeared after 21 h. In two 700 °C experiments of Huang and Wyllie (1986), the phase assemblage was the same in runs of 40 and 63 h, with loss of quartz and growth of garnet and minor clinopyroxene.

The liquidus temperature for the dehydrated tonalite at this pressure is estimated to be near 1250 °C, following

Green's (1972) result for a similar composition. The results in Figure 2 define the liquidus down to about 975 °C with 10% H₂O, with garnet as the primary liquidus mineral from near 975 °C, and 7–8 wt% H₂O to at least 1150 °C, and 3% H₂O, and liquidus amphibole for H₂O contents greater than about 8–9%. The amphibole-out curve falls from about 975 °C at the liquidus to below 950 °C with 5% and 2.5% H₂O. For the same tonalite with no H₂O added, however, Rutter and Wyllie (1988) bracketed amphibole-out between 950 and 1000 °C. Their experiment of 4-d duration at 950 °C yielded relict hornblende surrounded by growth of a new amphibole of different composition, indicating that amphibole is stable. We conclude that the amphibole-out curve in Figure 2 remains close to 950 °C. The steeply sloping plagioclase-out curve seems to be well defined according to the experiments of longest duration. As reported by Huang and Wyllie (1986), clinopyroxene is present "only in minor amounts except near the liquidus," where it becomes the

TABLE 3. Experimental conditions and results

No.	T (°C)	t (h)	H ₂ O added	Products*
78	950	71.0	2.6	Gl, Ga, Cpx, Pl, Rut, (Qtz?), Ox
71	1000	24.0	2.5	Gl, Ga, (Cpx), Pl, Qtz, Rut, Ox
93	1000	60.0	2.5	Gl, Ga, Cpx, (Pl), (Qtz?)
77	1050	46.0	2.4	Gl, Ga, Cpx, (Pl?)
92	1100	30.0	2.4	Gl, Ga
610**	700	63.0	5.0	Gl, Ga, Cpx, Hb, Pl, Bi
602**	800	30.0	5.0	Gl, Ga, Cpx, Hb, Pl, Bi
64	850	24.0	5.0	Gl, Ga, Cpx?, Hb, Pl, Rut, Apa, Zir
63	900	21.0	4.6	Gl, Ga, Cpx, Hb, (Pl?), Apa, Zir
28	950	16.5	5.2	Gl, Ga, Cpx, (Hb?)
30	1000	8.0	5.2	Gl, Ga, (Cpx)
29	1040	5.0	5.1	Gl, Ga
68	1060	3.5	5.0	Gl, Ga, (r-Cpx)
105	975	12.0	7.6	Gl, Ga, Cpx, (Hb)
106	1025	19.0	7.4	Gl
65	850	26.0	10.0	Gl, Hb, Ga, Cpx, Apa, Zir, Ti
42	900	14.0	9.0	Gl, Hb, Ga, Ox, (Cpx)
45	950	10.0	8.9	Gl, Hb, Ox
41	1000	5.0	9.5	Gl

* Gl = glass, Ga = Garnet, Cpx = Ca-rich pyroxene, Hb = amphibole, Ox = Fe-Ti oxide phase, Pl = plagioclase feldspar, Rut = rutile, Zir = zircon, Apa = apatite, Ti = titanite; phases in parentheses indicate trace amount present; a question mark signifies uncertainty about whether the phase is stable; a letter "r" indicates phase interpreted as relict and not stable.

** Two runs done in Au capsules, from Huang and Wyllie (1986).

primary mineral in their experiments. In this study, using Au capsules, clinopyroxene is not found on the liquidus in experiments with more than 2.5% H₂O added, although it does appear within 50 °C of the garnet liquidus. The clinopyroxene-out curve remains somewhat uncertain, however, being based on identification of trace amounts of the mineral or its absence. This may account for the irregularity in the clinopyroxene liquidus curve near 7.5% H₂O, although it is possible that there is some reaction associated with garnet and hornblende that affects clinopyroxene stability in this region. The biotite-out curve is bracketed with 5% H₂O at 800 to 825 °C, and the curves for quartz-out and orthoclase-out are situated at H₂O contents of less than 5% at 700 °C.

The broader pattern of phase relationships for tonalite-H₂O is illustrated in Figure 2b, with the use of our new results in the vapor-absent region and the reconnaissance results from Figure 1. Additional limits are provided by the data of Rutter and Wyllie (1988) for the solidus, orthoclase-out, and quartz-out for the tonalite with no water added (0.8 wt% H₂O). The phase boundaries are extended to 0% H₂O between solidus and liquidus using data from Green (1972) for an andesite composition similar to that of the dehydrated tonalite. For Green's (1972) composition, plagioclase and pyroxene coexist at the liquidus, and

TABLE 4. Microprobe analyses of products

Phase (n)	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	Total
Experiment 78										
Gl (5)	68.1(17)	0.5(5)	17.6(24)	1.2(16)	<0.1	0.4(3)	2.5(22)	6.41(5)	3.11(2)	92.2
Ga (6)	38.11(33)	1.69(15)	21.32(31)	20.06(53)	0.58(6)	6.99(56)	10.88(67)	0.09(1)	0.01(1)	99.74
Cpx (6)	48.23(53)	1.21(18)	12.08(60)	6.63(48)	0.09(2)	10.18(28)	19.29(23)	1.90(9)	0.04(2)	99.65
Pl (6)	57.49(121)		26.56(73)	0.20(4)			8.32(82)	6.77(51)	0.24(7)	99.62
Experiment 71										
Gl (3)	69.0(5)	0.6(3)	16.5(12)	1.8(14)	<0.1(10)	0.7(10)	3.0(07)	4.8(15)	3.4(16)	94.2
Ga (8)	38.66(80)	1.91(34)	21.28(39)	20.60(105)	0.57(8)	9.06(37)	7.78(42)	0.13(7)	0.05(7)	100.40
Cpx (7)	49.84(24)	0.99(7)	9.34(66)	8.48(97)	0.15(5)	11.49(38)	17.79(128)	1.55(5)	0.10(3)	99.73
Pl (5)	56.62(114)		27.12(89)	0.27(8)			8.99(91)	6.31(53)	0.25(9)	99.58
Experiment 93										
Gl (4)	67.2(54)	0.8(12)	17.3(17)	1.7(10)	0.1(7)	0.9(7)	3.9(17)	5.1(12)	2.9(13)	93.4
Ga (8)	38.66(46)	1.76(26)	1.47(38)	20.22(95)	0.60(9)	9.22(69)	8.35(39)	0.09(4)	0.03(2)	100.39
Cpx (9)	49.35(34)	1.06(7)	10.21(30)	6.90(54)	0.11(3)	11.14(25)	19.14(84)	1.72(4)	0.05(4)	99.68
Pl (6)	57.37(67)		26.62(52)	0.25(2)			8.49(43)	6.52(28)	0.32(5)	99.62
Experiment 77										
Gl (5)	64.6(68)	0.7(6)	18.2(26)	2.8(13)	<0.1(8)	1.2(4)	5.0(15)	4.9(27)	2.5(22)	94.7
Ga (7)	39.45(34)	1.38(27)	20.92(32)	18.48(62)	0.60(5)	11.89(58)	7.35(30)	0.09(2)	0.01(1)	100.16
Cpx (6)	49.31(91)	0.94(12)	11.55(48)	6.65(91)	0.11(2)	10.39(46)	19.00(74)	1.66(10)	0.01(4)	99.76
Experiment 92										
Gl (5)	61.3(42)	0.8(3)	18.3(21)	4.6(10)	<0.1(7)	2.4(4)	6.0(13)	4.0(31)	2.1(4)	95.2
Ga (9)	40.01(45)	0.84(42)	22.45(64)	15.95(73)	0.58(5)	12.91(60)	7.36(40)	0.05(2)	0.00(2)	100.22
Experiment 64										
Pl (7)	58.27(112)		25.64(89)	0.42(18)			7.75(78)	6.70(40)	0.38(13)	99.28
Experiment 63										
Pl (6)	55.87(79)		27.66(62)	0.25(3)			9.61(67)	6.05(32)	0.23(6)	99.69

Note: abbreviations are Gl = glass, Ga = garnet, Cpx = clinopyroxene, Pl = plagioclase; numbers in parentheses after phase identification indicate number of analyses included in reported averages. Glass analyses have been recalculated to 100% totals. Totals given in this table are original totals, reflecting presence of H₂O in the glass. Numbers in parentheses in body of table are standard deviations in hundredths of percent for the reported averages.

* Total iron as FeO.

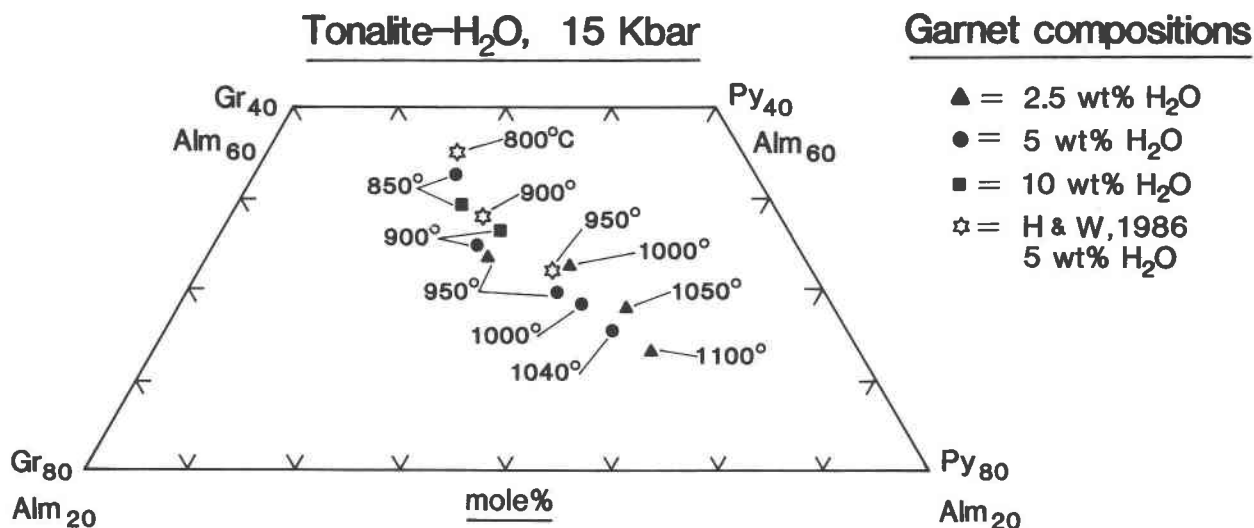


Fig. 3. Compositions of experimental garnets plotted in the grossular-almandine-pyrope (Gr-Alm-Py, respectively) triangle. Each point represents the average of two to nine electron microprobe analyses. Temperatures at which the garnets were grown are indicated, and the results of Huang and Wyllie (1986) at 800–950 °C are shown by open stars.

pyroxene is the liquidus mineral with 5% H₂O, joined by garnet some tens of degrees below the liquidus (compare Figs. 1 and 2). Our results are consistent with clinopyroxene as the liquidus mineral in the range 0–3% H₂O, but we find garnet or amphibole on the liquidus at higher H₂O contents. The near-liquidus relationships for calc-alkaline compositions near tonalite and andesite with low H₂O are sensitive to water content as well as to variations in bulk composition.

As already stated in connection with Figure 1, the positions of the phase boundaries at H₂O contents higher than those examined in this study need some adjustment for Fe loss to the AgPd alloy or Pt capsules used in previous work. Major trends are clear, however, with the data available. Figure 2b shows that the major effect of water on tonalite phase relations is depression of the liquidus and phase boundaries for anhydrous silicate minerals, eventually resulting in the stabilization of liquidus amphibole at H₂O contents above 8 to 9 wt%. The breakdown temperatures of amphibole and biotite in the vapor-absent region in the presence of hydrous melt change little as a function of H₂O content compared with the observed changes for the anhydrous silicates. The subsolidus assemblage according to Huang and Wyllie (1986) is Hb + Cpx + Pl + Qz + Ga + Bi + V. The 4% orthoclase in the original rock is dissolved in the vapor phase at this pressure (Stern et al., 1975). At low H₂O contents, some orthoclase must be present, and it has been observed in the vapor-free rock, with the orthoclase-out curve bracketed at 850–875 °C (Rutter and Wyllie, 1988). At temperatures below about 650 °C, additional clinopyroxene would be produced in the subsolidus assemblage, associated with the breakdown of plagioclase to jadeite (Lambert and Wyllie, 1974).

Mineral compositions

Microprobe-analysis data for minerals and quenched melts in experiments with 2.5 wt% H₂O added are in Table 4. Analytical data for experiments with 5 or 10 wt% H₂O added are given in Carroll and Wyllie (1989).

Garnet. The Ca-Mg-Fe compositions of experimental garnets and the temperatures at which they are grown are shown in Figure 3. Also shown as stars are garnet compositions at 800 to 950 °C reported by Huang and Wyllie (1986). The garnets range from Gr_{19.5}Py_{47.5}Alm₃₃ at 1100 °C and 2.5% H₂O to Gr_{29.5}Py_{21.2}Alm_{49.3} at 850 °C and 10% H₂O. With decreasing temperature, garnets have higher FeO, lower MgO, and slightly higher CaO contents. Variations in garnet Mg/(Mg + Fe), where Fe represents total Fe as Fe²⁺, with temperature and amount of water in the system are shown in Figure 5, with the general trend of lower Mg/(Mg + Fe) at lower temperature. The Mg/(Mg + Fe) values range from a maximum of 0.60 at 1100 °C, 2.5% H₂O, to a minimum near 0.25 at 850 °C and 5% H₂O. The 2.5% and 5% H₂O experiments show at most a 10% difference in Mg/(Mg + Fe) at constant temperature, with the experiments at lower contents of water having the lower Mg/(Mg + Fe) garnets.

The concentrations of the minor components Ti, Mn, and Cr in the garnets are all low, and abundances decrease in the order Ti > Mn >> Cr. On a weight-percent basis, TiO₂ varies from 0.84 to 1.91%, MnO from 0.57 to 1.3%, and Cr₂O₃ is less than 0.05%. The total minor-element content is never more than 2.5 wt%, and there are no systematic variations with either temperature or amount of water in the system except for a tendency for the lower temperature garnets to have slightly higher Ti and Mn contents.

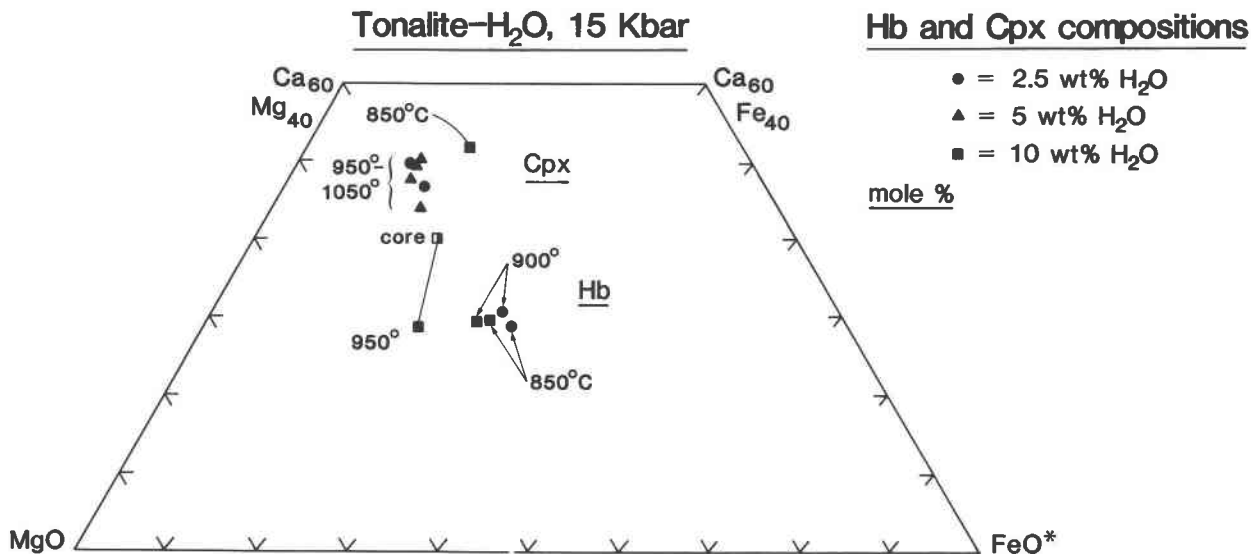


Fig. 4. Clinopyroxene and hornblende compositions plotted in the triangle MgO-CaO-FeO. The sample labeled "core" shows the composition of relict clinopyroxene core and surrounding euhedral hornblende crystal.

Clinopyroxene. Ca-rich clinopyroxene was the only pyroxene encountered in this study. The average Ca-Mg-Fe compositions of the pyroxenes are shown in Figure 4 and analyses are given in Table 4. The (small) effects of temperature and water content on pyroxene Mg/(Mg + Fe) are shown in Figure 5. The clinopyroxenes show little change in Mg/(Mg + Fe) or Ca/(Mg + Fe) with temperature or water content of the system, although the clinopyroxene at 850 °C and 10% H₂O is slightly richer in Ca. Nonquadrilateral components in the clinopyroxenes range from 9 to 12 mol% Ca-Tschermak's molecule and 5 to 11 mol% jadeite.

Abundances of the minor elements Ti, Mn, and Cr decrease in the order Ti ≫ Mn > Cr, with Cr₂O₃ always less than 0.05 wt%, MnO between 0.07 and 0.15 wt%, and TiO₂ from 0.9 to 1.45 wt%. TiO₂ shows a small increase with decreasing temperature, whereas the Cr and Mn variations are within the analytical error. Na and Al in the experimental pyroxenes are significant components, and they are both slightly enriched in the pyroxenes grown at lower temperatures. Abundances range from 9.34 to 12.08 wt% for Al₂O₃ and from 1.22 to 2.33 wt% for Na₂O.

Amphibole. Amphibole was observed only in experiments with 5 or 10 wt% H₂O and then only at temperatures below 975 °C. Amphibole compositions are plotted along with those of clinopyroxene in Figure 4. The Mg/(Mg + Fe) of amphibole is higher than that of coexisting garnet and lower than that of coexisting clinopyroxene, as shown in Figure 5. Several experiments had well-formed amphiboles with relict cores of clinopyroxene or clinopyroxene partly altered to amphibole. The amphibole rims were homogeneous as far as could be determined, and they were easily discerned in backscattered

electron images. The rim and core compositions of an amphibole grown at 950 °C and 10% H₂O added are shown in Figure 4; other compositions plotted in Figure 4 all correspond to rim compositions. According to the classification scheme of Leake (1978) the amphiboles are pargasites. At 850 °C, amphiboles grown from charges with 10% H₂O have higher Ca/Mg and lower FeO than amphiboles found in the 5% H₂O experiments.

Minor elements in the amphiboles decrease in the order Ti > Mn > Cr, with TiO₂ ranging from 1.03 to 1.79 wt%, MnO from 0.17 to 0.32 wt%, and Cr₂O₃ at the level of detection (<0.05 wt%). TiO₂ is slightly higher in the higher temperature amphiboles, but MnO shows no systematic variation. Alkalis in the amphibole together range from 2.77 to 3.58 wt%, and the amphiboles from the 10% H₂O experiments have the highest alkali contents. Molar Na/K ratios are ~3, similar to or slightly lower than the coexisting liquid but not varying significantly with temperature or amount of water in the system.

Melt compositions

Microprobe analyses of quenched melts from experiments with 2.5% H₂O added, recalculated on a water-free basis, are in Table 4. Other quenched melt analyses are reported in Carroll and Wyllie (1989). Each analysis represents an average of three to eight separate analyses. Evidence that the glass compositions are representative of the melt present at high pressures and temperatures includes compositional homogeneity of glass throughout the experimental charges, lack of significant quench overgrowths on minerals grown during the experiments, and the identical glass compositions in crystal-rich and crystal-free regions of experiments showing evidence of crystal settling.

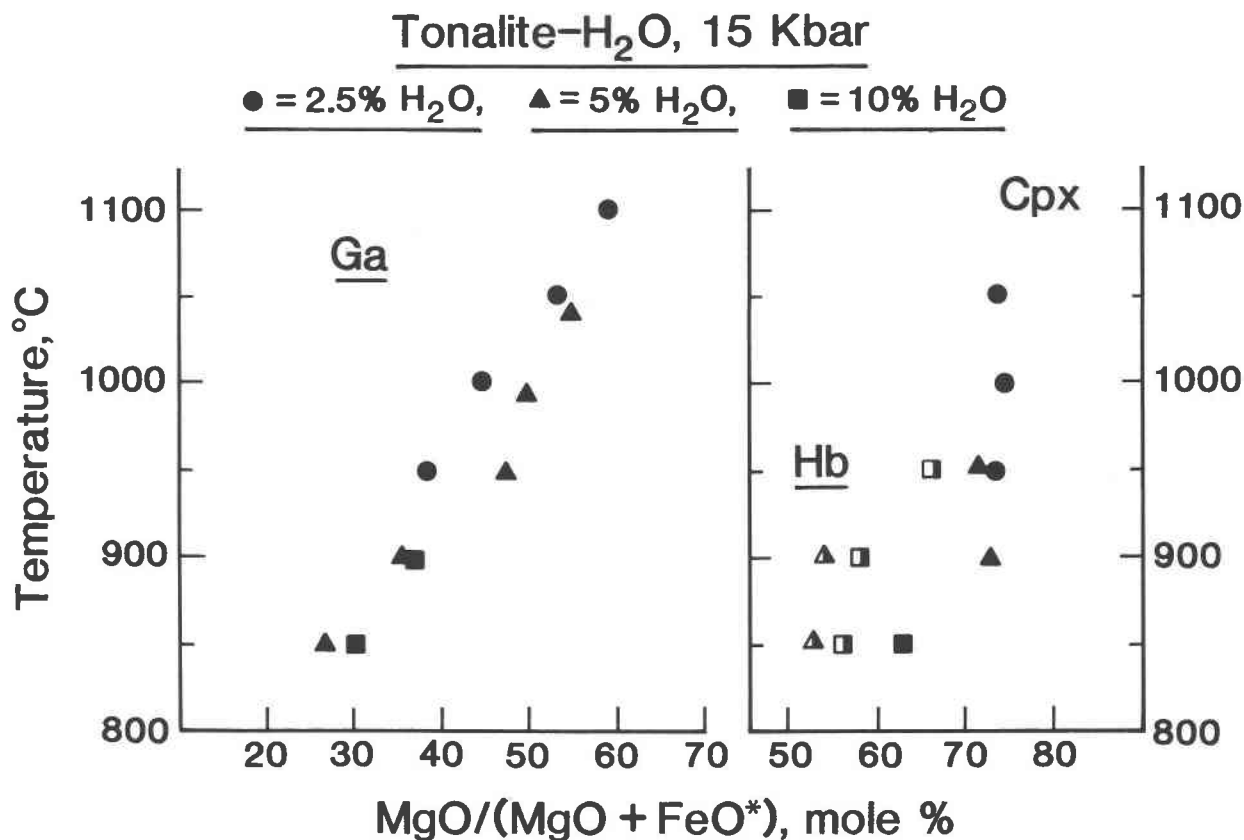


Fig. 5. Variations in molecular Mg/(Mg + Fe) with experimental temperature for (a, left) garnets and (b, right) hornblende (half-filled symbols) and clinopyroxene.

Variations in glass composition are plotted as a function of temperature in Figure 6. The three lines on each plot correspond to tonalite with added H₂O equal to 2.5, 5, or 10 wt% (circles, triangles, and squares, respectively). The small arrow on the weight-percent axis of each diagram indicates the composition of the tonalite starting material. The glass analyses show compositions corresponding to the starting materials at super-liquidus temperatures (Table 3), and the smooth compositional trends with increasing temperature correspond to an increasing degree of melting of the crystalline starting material. The melts become poorer in SiO₂, K₂O, and Na₂O and richer in CaO, MgO, FeO, and TiO₂ as the temperature increases. The larger amount of melting at a given temperature for the more water-rich bulk compositions is reflected in lower alkali and silica concentrations in the melt. The destabilization of plagioclase by H₂O results in more Al₂O₃-enriched melts at lower temperatures in the more water-rich experiments. The observed trends in the alumina content of the melt indicate that plagioclase melts between 1000 and 1050 °C for the 2.5% H₂O experiments and between 850 and 900 °C for the 5% H₂O experiments, which is in good agreement with the mineral assemblages observed in the experiment products. The low Al₂O₃ point for 2.5% H₂O at 1000 °C is from a short duration exper-

iment that contained relict plagioclase, which results in a more alumina-depleted melt. The high Na₂O content of the 850 °C and 10% H₂O experiment reflects the lack of plagioclase crystallization in this sample owing to the high water content.

When plotted in terms of SiO₂ content, the melt compositions, except for Al₂O₃ and to a lesser extent MgO, show essentially collinear trends irrespective of the amount of water present. Al₂O₃ is strongly influenced by the abundance of plagioclase or garnet, the most Al-rich phases. The 10% H₂O experiments, with liquidus hornblende, have the highest alumina contents, the 5% H₂O experiments have intermediate alumina, and the 2.5% H₂O experiments have the lowest alumina in the melt (at <~1025 °C). The predominance of Mg-rich amphibole in the 10% H₂O starting composition also produces melts with lower MgO at fixed SiO₂ content compared to the lower H₂O samples.

Glass compositions, shown as filled symbols, are plotted in the triangle CaO-MgO + FeO-1/4SiO₂ in Figure 7. The composition of the tonalite starting material is coincident with the square at the low-SiO₂ (high-temperature) end of the plotted analyses. The open symbols in Figure 7 show the compositions of calc-alkaline gabbro through granite from the Sierra Nevada batholith (from Carmi-

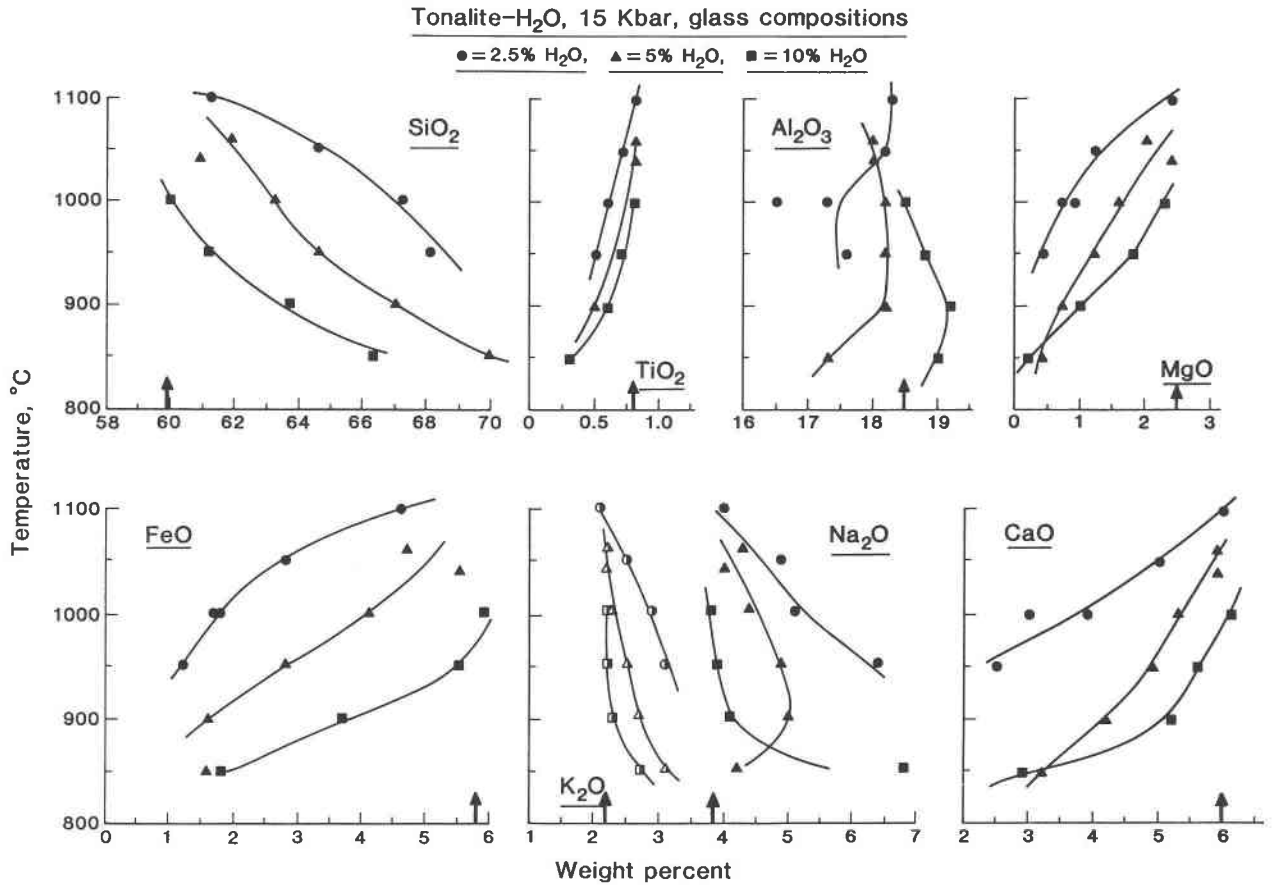


Fig. 6. Major element analyses of quenched melts in tonalite + H₂O system at 15 kbar as a function of experimental temperature. Samples with different amounts of added water are shown by different symbols, as indicated in legend. Small arrows on the wt% axis show the composition of tonalite starting material.

chael et al., 1974, page 560; similar trends are observed for calc-alkaline volcanic rocks). The experimental glass compositions all project onto a single curving path, independent of H₂O content, but clearly diverging from the calc-alkaline batholith trend. The same observation about the non-calc-alkaline nature of melts at 15 kbar was made by Huang and Wyllie (1986) for three samples of tonalite + 5% H₂O equilibrated at 800 to 950 °C. Stern and Wyllie (1978) noted similar departures of experimental melt compositions from the calc-alkaline trend in experiments on gabbro and tonalite at 30-kbar pressure.

Compositional fields for the coexisting minerals in the experiments are in the lower portion of Figure 7. Garnet is the mineral showing the largest variation in Ca/(Mg + Fe), with the highest-temperature garnets being the most Ca-poor. Hornblende and clinopyroxene show much less variation in Ca/(Mg + Fe), and the compositional variation cannot be correlated with the temperature or water content of the coexisting melt. The geometric relationships among the plotted melts and coexisting mineral compositions clearly indicate the role of garnet crystallization (or hornblende, in 10% H₂O experiments) in determining the near-liquidus compositional evolution of

tonalitic melt; i.e., garnet (or hornblende) subtraction drives melts toward higher Ca/(Mg + Fe).

PETROLOGICAL APPLICATIONS

Estimated crustal thicknesses in mature continental arc regions range from approximately 70 km in the Andes, to 45 km in western North America, to 30–35 km in Alaska (Gill, 1981, p. 48). The phase relationships established at 15 kbar, corresponding to a depth of approximately 50 km, are thus applicable to magmatic processes at deep-crustal to upper-mantle depths in regions of plate convergence. Although mounting evidence from detailed petrological and geochemical studies documents the multiple-source, open-system nature of magmatic processes (e.g., Arculus and Powell, 1986; Marsh, 1987; Hildreth and Moorbath, 1988), the experimental determination of phase stabilities and compositions provides the basis for prediction of possible magma-source materials and plausible differentiation trends or parent-daughter relations in a given magmatic suite. Our results are concentrated in the water-undersaturated portion of the tonalite-H₂O system at 15 kbar, and they complement and build upon the previous work of Huang and Wyllie (1986).

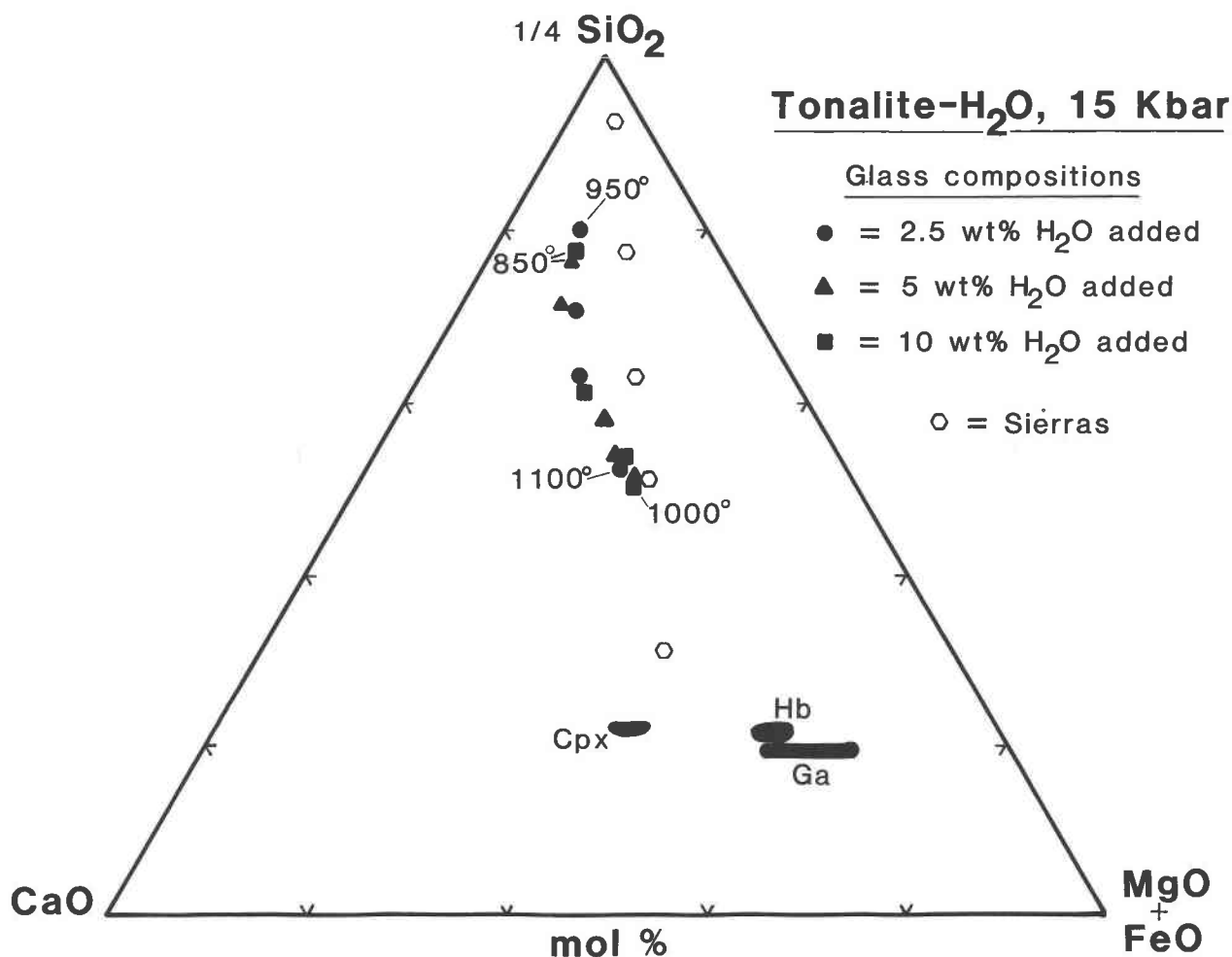


Fig. 7. Compositions of quenched melts and crystals from tonalite with 2.5 to 10% H₂O at 15 kbar. Open symbols show the compositions of Sierra Nevada gabbro through granite. Filled fields in the lower part of diagram indicate projected compositions of clinopyroxene (Cpx), hornblende (Hb), and garnet (Ga).

Amphibole fractionation

The possible role of amphibole fractionation in the genesis of calc-alkaline rocks, a topic of long-standing debate, was reviewed in Huang and Wyllie (1986). New results on tonalite at 15 kbar show amphiboles with significantly higher Mg/(Mg + Fe) than the coexisting andesitic to dacitic or rhyodacitic melts [100 Mg/(Mg + Fe) = 55 to 65 in amphiboles versus 35 to 45 in quenched melts], suggesting that amphibole fractionation at high pressure may not be effective in inhibiting Fe enrichment in andesitic and more evolved liquids. Clinopyroxene is even more Mg rich than amphibole, and thus fractionation of garnet with low Mg/(Mg + Fe) ratios is the most important factor inhibiting Fe enrichment of melts under the investigated conditions. These observations are in accord with the previous results of Huang and Wyllie as well as those of Allen and Boettcher (1983) on more mafic melt compositions. This finding contrasts with the proposed role of amphibole fractionation for inhibiting Fe

enrichment as suggested by Green (1982) on the basis of data showing amphibole with Mg/(Mg + Fe) much closer to that of the coexisting andesitic liquid. It is also notable that more than 8 wt% H₂O is required to stabilize liquidus or near-liquidus amphibole in andesite melt at 950 to 975 °C. Such a large amount of water is only likely in magmas produced by low degrees of melting, and they would be considerably more silicic than andesite. This restriction suggests that magmas of andesitic affinity at 15-kbar depths would contain mainly garnet and clinopyroxene, with amphibole appearing at lower temperatures, coexisting with a more silicic melt (~65 wt% SiO₂).

Magma differentiation and production at 15 kbar

Fractionation of andesite or tonalite at 15 kbar predominantly involves garnet and clinopyroxene near the liquidus and amphibole and plagioclase at lower temperatures, depending somewhat on water content, as shown in Figure 3. Glass compositions in partially crystalline tonalite are significantly different from typical calc-alka-

line rocks, such as those in the Sierra Nevada of western North America (e.g., see Fig. 7). The deviation of the glass compositions from the calc-alkaline trend is toward higher Ca/(Mg + Fe), as was indicated by the exploratory results of Huang and Wyllie (1986). The departure of melt compositions from the almost constant Ca/(Mg + Fe) ratio of the calc-alkaline trend is greater than that observed in the previous study, and only at temperatures less than 850 °C might liquids (granitic) from partially molten tonalite approach calc-alkaline compositions in terms of the Ca/(Mg + Fe) ratio. The experimental melts are also generally richer in Al₂O₃ than typical calc-alkaline rocks, and fractional crystallization at shallower levels with more significant involvement of plagioclase is required to explain the compositions of most arc magmas (e.g., see Grove and Baker, 1984). In cases requiring involvement of garnet in magma genesis, such as in the Andes of central Chile (Hildreth and Moorbath, 1988), a complex history involving polybaric fractionation is needed to produce the appropriate major-element compositions.

Our conclusions regarding crystal fractionation at 15 kbar and the genesis of calc-alkaline magmas are also applicable to partial melting of tonalitic to gabbroic rocks in thickened crust. Such processes have been discussed at length by Wyllie (1977), Burnham (1979), and Huang and Wyllie (1986). The near-liquidus mineral assemblages of Ga + Cpx ± Hb (Fig. 3) observed in experiments on tonalite + H₂O may be interpreted as potential residues from which andesitic melt could be extracted, assuming that (1) melting was not extensive enough to have consumed a mineral and (2) the melt was not in a reaction relationship with any mineral. However, the work of Hellman (1979; in Green, 1982) and Huang and Wyllie (1986) indicates that partial melts from hydrous basalt at 15 kbar do not correspond to calc-alkaline compositions, having inappropriately high Ca/(Mg + Fe) ratios and Al₂O₃ enrichments. Our results further show that liquids produced in the melting interval of tonalite with 3 to 11 wt% H₂O at 15 kbar follow a compositional path with distinctly higher Ca/(Mg + Fe) and Al₂O₃ compared to typical calc-alkaline rocks (Fig. 7). The implication of these observations is that partial fusion of garnet-bearing tonalite to gabbro in the deep crust will not produce calc-alkaline melts.

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REFERENCES CITED

- Allen, J.C., and Boettcher, A.L. (1978) Amphiboles in andesite and basalt: II. Stability as a function of P - T - f_{H_2O} - f_{O_2} . *American Mineralogist*, 63, 1074-1087.
- (1983) The stability of amphibole in andesite and basalt at high pressures. *American Mineralogist*, 68, 307-314.
- 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.
- Arculus, R.J., and Powell, R. (1986) Source component mixing in the regions of arc magma generation. *Journal of Geophysical Research*, 91, 5913-5926.
- Bateman, P.C., Clark, L., Huber, N.K., Moore, J.G., and Rinehart, 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., and Wyllie, P.J. (1968) Jadeite stability measured in the presence of silicate liquids in the system NaAlSi₃O₈-SiO₂-H₂O. *Geochimica et Cosmochimica Acta*, 32, 999-1012.
- 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.
- Burnham, C.W. (1979) Magmas and hydrothermal fluids. In H.L. Barnes, Ed., *Geochemistry of hydrothermal ore deposits*, p. 71-136. Wiley, New York.
- Carmichael, I.S.E., Turner, F.J., and Verhoogen, J. (1974) *Igneous petrology*. McGraw-Hill, New York.
- Carroll, M.R., and Wyllie, P.J. (1989) Experimental phase relations in the system tonalite-peridotite-H₂O. Implications for assimilation and differentiation processes near the crust-mantle boundary. *Journal of Petrology*, 30, 1351-1382.
- Eggler, D.H., and Burnham, C.W. (1973) Crystallization and fractionation trends in the system andesite-H₂O-CO₂-O₂ at pressures to 10 kbar. *Geological Society of America Bulletin*, 84, 261-271.
- Gill, J.B. (1981) *Orogenic andesites and plate tectonics*. Springer-Verlag, New York.
- Green, T.H. (1972) Crystallization of calc-alkaline andesite under controlled high pressure hydrous conditions. *Contributions to Mineralogy and Petrology*, 34, 150-166.
- (1982) Anatexis of mafic crust and high pressure crystallization of andesite. In R.S. Thorpe, Ed., *Andesites: Orogenic andesites and related rocks*, p. 465-487. Wiley, Chichester, England.
- Green, T.H., and Ringwood, A.E. (1968) Genesis of the calc-alkaline igneous rock suite. *Contributions to Mineralogy and Petrology*, 18, 105-162.
- Grove, T.L., and Baker, M.B. (1984) Phase equilibrium controls on the tholeiitic vs. calc-alkaline differentiation trends. *Journal of Geophysical Research*, 89, 3253-3274.
- Grove, T.L., and Kinzler, R.J. (1986) Petrogenesis of andesites. *Annual Reviews of Earth and Planetary Sciences*, 14, 417-454.
- Hildreth, W., and Moorbath, S. (1988) Crustal contributions to arc magmatism in the Andes of central Chile. *Contributions to Mineralogy and Petrology*, 98, 455-489.
- Huang, W.-L., and Wyllie, P.J. (1986) Phase relationships of gabbro-tonalite-granite-water at 15 kbar with applications to differentiation and anatexis. *American Mineralogist*, 71, 301-316.
- Lambert, I.B., and Wyllie, P.J. (1974) Melting of tonalite and crystallization of andesite liquid with excess water to 30 kbar. *Journal of Geology*, 82, 88-97.
- Leake, B.E. (1978) Nomenclature of amphiboles. *Canadian Mineralogist*, 16, 501-520.
- Marsh, B. (1987) Magmatic processes. *Reviews in Geophysics*, 25, 1043-1053.
- Piwinskii, A.J. (1973) Experimental studies of igneous rock series, central Sierra Nevada batholith, California, Part II. *Neues Jahrbuch für Mineralogie, Monatshefte*, 193-215.
- Rutherford, M.J., Sigurdsson, H., Carey, S., and Davis, A. (1985) The May 18, 1980, eruption of Mount St. Helens 1. Melt composition and experimental phase equilibria. *Journal of Geophysical Research*, 90, 2929-2947.
- Rutter, M.J., and Wyllie, P.J. (1988) Melting of vapour-absent tonalite at 10 kbar to simulate dehydration melting in the deep crust. *Nature*, 331, 159-160.
- Sekine, T., and Wyllie, P.J. (1982) The system granite-peridotite-H₂O at

- 30 kbar, with applications to hybridization in subduction zone magmatism. *Contributions to Mineralogy and Petrology*, 81, 190–202.
- Spencer, K.J., and Lindsley, D.H. (1981) A solution model for coexisting iron-titanium oxides. *American Mineralogist*, 66, 1189–1201.
- Stern, C.R., and Wyllie, P.J. (1973) Melting relations of basalt-andesite-rhyolite-H₂O and a pelagic red clay at 30 kbar. *Contributions to Mineralogy and Petrology*, 42, 313–323.
- (1978) Phase compositions through crystallization intervals in basalt-andesite-H₂O at 30 kbar with implications for subduction zone magmas. *American Mineralogist*, 63, 641–663.
- Stern, C.R., Huang, W.-L., and Wyllie, P.J. (1975) Basalt-andesite-rhyolite-H₂O: Crystallization intervals with excess H₂O and H₂O-undersaturated liquidus surfaces to 35 kilobars, with implications for magma genesis. *Earth and Planetary Science Letters*, 28, 189–196.
- Wyllie, P.J. (1977) Crustal anatexis: An experimental review. *Tectonophysics*, 43, 41–71.
- (1979) Magmas and volatile components. *American Mineralogist*, 64, 469–500.

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