

EXPERIMENTAL TESTING OF "EQUILIBRIUM" PARTIAL MELTING OF PERIDOTITE UNDER WATER-SATURATED, HIGH-PRESSURE CONDITIONS

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ABSTRACT

Experimental aspects of studies of water-saturated melting of peridotite compositions are reviewed and it is shown that problems of grain size of starting materials, extent of iron loss, iron oxidation state, and problems of electron probe microanalysis need to be evaluated. The reality of quench outgrowth and nucleation of phases during quenching of high-pressure runs is demonstrated and the method of determination of equilibrium liquid by analysis of glasses in quenched runs is shown to give erroneous results for wet melting of peridotite. The use of bulk and mineral compositional data, together with crystal/liquid partition data, to calculate equilibrium melt compositions in favorable cases is shown to yield reliable results. This is demonstrated by reversal experiments in which the liquidus temperatures and phases of the postulated melt match with the residual phases of the peridotite at the appropriate pressure and temperature.

Water-saturated melting of peridotitic compositions in island arc environments will produce parental basalts of magnesian quartz tholeiite (10 kbar, 1100-1200°C) to olivine tholeiite composition (20 kbar, 1100-1200°C) with 25-35% melting. Lower degrees of melting at 10-20 kbar will only produce more undersaturated magmas with higher normative olivine or nepheline contents. Andesites or dacites are not possible melting products of peridotitic source rocks at depths greater than 30 km.

SOMMAIRE

L'aspect expérimental d'études effectuées sur la fusion de péridotites en présence d'eau est étudiée et la conclusion qu'on en tire est celle-ci: il faut réévaluer les problèmes de la dimension des grains des matériaux de départ, de la perte du fer, de l'état d'oxydation du fer et des problèmes de microanalyse à la sonde électronique. Nous pouvons démontrer la réalité de l'excroissance trempée et de la nucléation de nouvelles phases pendant la trempe d'essais à haute pression; on y démontre aussi que la pratique de déterminer le liquide d'équilibre par l'analyse de verres (liquides trempés) donne des mauvais résultats en cas de fusion par voie humide de la péridotite. Par contre, on obtient de bons résultats en utilisant les données de composition minéralogiques et les données sur les répartitions cristal/liquide pour calculer les compositions de liquides d'équilibre dans des cas favorables. Ceci peut se

démontrer dans plusieurs expériences "renversées" pendant lesquelles les températures du liquidus et les phases sur le liquidus en question correspondent aux phases résiduelles de la péridotite à des températures et pressions appropriées. La fusion de péridotites en milieux saturés en eau, comme dans les arcs insulaires, produira des basaltes du genre tholéiite quartzique magnésien (10 kbar, 1100-1200°C) ou tholéiite à olivine (20 kbar, 1100-1200°C) avec une fusion de 25 à 35%. Une fusion moins poussée, soit 10-20%, produira uniquement des magmas sous-saturés contenant plus d'olivine normative ou de néphéline. Les andésites ou dacites ne peuvent provenir de péridotites par fusion partielle à des profondeurs plus grandes que 30 km.

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INTRODUCTION

The melting behavior of peridotitic compositions under water-saturated conditions at high pressure has become a matter of controversy amongst experimental petrologists. Rather diametrically opposed interpretations of apparently simple experiments make it easy for the non-specialist to adopt the viewpoint that anything remains possible as a melting product of the upper mantle and it must appear to many earth scientists that hypotheses of magma genesis can remain unconstrained by knowledge of mantle melting behavior under water-saturated conditions. A principal controversy is whether siliceous (>55% SiO₂), highly quartz-normative liquids can be derived as equilibrium partial melts of peridotite at pressures >10 kbar, under water-saturated conditions. A recent paper by Nehru & Wyllie (1975) illustrates the problems but in reporting their own data and emphasizing the experimental difficulties encountered, these authors do not equally emphasize that these experimental difficulties have been foreseen, and minimized or surmounted by other groups using different approaches.

PROBLEMS AND COMPARISONS IN EXPERIMENTAL METHODS

Four separate laboratories (Kushiro *et al.* 1968, 1972; Mysen & Boettcher 1975a; Nehru &

Wyllie 1975; and Green 1972, 1973a,b) have studied the melting relationships of peridotitic compositions under water-saturated conditions. In three studies (Kushiro *et al.* 1968; Milhollen *et al.* 1974 and Nehru & Wyllie 1975; and Green 1972, 1973) the solidus was placed between 950°C and 1000°C at 5 to 30 kbar. Mysen & Boettcher (1975a,b) placed solidi for four peridotite compositions at much lower temperatures (<800°C at 25-30 kbar for the least-refractory compositions). The detection of the solidus was based in the first instance in *all* the investigations on the optical examination of the charge and included textural changes indicating the appearance of an intergranular melt phase. Additional criteria include the identification of quenched glass and the distinction of quenched glass derived from the silicate dissolved in the vapor phase from that derived from a silicate melt. These observations are subjective and Green (1973a) attempted to obtain an objective result by analyzing amphibole compositions above and below the optically determined solidus. It was shown that the amphibole changed in Na/K and Ti/K across the 'solidus' with the higher temperature amphibole having lower K₂O contents. Furthermore, knowledge of the bulk composition and coexisting mineral compositions at 10 kbar and 1000°C and 970°C, showed that at 1000°C another phase (additional to olivine, pyroxenes and amphibole) was required with a higher K/Na ratio than all the crystalline phases — this phase was correlated with the optically observed intergranular melt phase. No such phase was required, however, in the 970°C run and the compositions of amphibole, pyroxene and olivine were such as to satisfy the bulk composition without requiring the presence of an additional K-enriched phase. Mysen & Boettcher (1975a, p. 533) did not give full cognizance to these bases on which Green (1973a) had determined the solidus at 10 kbar and published data (Mysen & Boettcher 1975b, Table 4, 1975a, Fig. 3) purporting to show *no* change in amphibole composition across their solidus (which they placed at 800-840°C). If the equilibrium solidus for Mysen & Boettcher's composition is at ~1000°C instead of ~820°C, then their only published analysis of above-solidus amphibole is that at 1100°C and is obviously very different (0.04% K₂O, 1.2% Na₂O) from those at lower temperatures (0.11-0.32% K₂O, 2.0-2.6% Na₂O). However, the real significance of these (and other) analyses in Mysen & Boettcher's work could only be gauged after a very careful microprobe study of the primary and secondary mineralogy in the natural rock starting materials. The samples used by Mysen & Boettcher (1975a,b)

in their study were natural rocks crushed to <200 mesh, i.e. mineral fragments (and aggregates) up to 70 microns diameter. I have repeated experiments on a natural lherzolite of known mineralogy (Frey & Green 1974) using identical run times, temperatures, and water content to those used by Mysen & Boettcher at 15 kbar on lherzolite B. These new data show persistence of zoned, unequilibrated relicts of primary minerals up to at least 1100°C and the only effect on primary minerals at temperatures <950°C appears to be minor solution-rounding of original mineral grains by the large amount of vapor phase (16-22 wt. % H₂O) present. Quench glass from the vapor phase forms thin films on most mineral grains. New growth of amphibole apparently occurs in some lower temperature runs but the dominance of relict, original mineral grains means that such new crystallization may reflect a local chemical system and certainly cannot be assumed to be equilibrium crystallization of the bulk composition.

The failure to reach equilibrium using natural mineral mixes was carefully documented by Råheim & Green (1974) using minerals ground to <10 microns and run times greatly in excess of those used by Mysen & Boettcher (1975a,b). It should be noted that any increase in reaction rates attributed to the presence of a free vapor phase results from a very effective increase in intergranular diffusion rates (Ahrens & Schubert 1975) and a free vapor phase is ineffective in increasing reaction rates controlled by intracrystalline diffusion of coarsely crystalline starting materials. A more detailed appraisal of the problems inherent in the use of coarsely crystalline starting materials will be published elsewhere based on detailed examination of melting relations of a natural lherzolite (~200 mesh) at 15 kbar, 870°C to 1200°C, water-saturated conditions. There are, however, several areas in which the experimental techniques normally used in the Canberra laboratory offer distinct advantages in reducing experimental uncertainties.

Nehru & Wyllie (1974) document the problem of iron loss in their melting runs at 20 kbar, 900°C-1250°C, and it is clear from their techniques that Mysen & Boettcher (1974a,b) must have similar iron losses which, when combined with the presence of relict starting materials, ensure that any use of Mg/Mg+Fe values in their charges must be highly suspect. Rather than the flattened pillow-shaped sample capsule containing 2-3mg of samples used by these groups, our own sample geometry remains cylindrical, and uses 10-20 mg of sample, recoverable as a coherent cylinder or series of discs which can be monitored for Fe-loss in tra-

verses from wall to wall. In subsolidus or near-solidus assemblages, Fe loss to container walls is limited and, under suitable run conditions, restricted to the marginal areas. In runs with a high proportion of melt, iron loss is pervasive throughout the charge (c.f. Nehru & Wyllie 1975) and the depletion of iron during such an experiment is commonly recorded in reverse zoning of olivine (or other) crystals from iron-rich core to magnesian margins (documented by Green & Ringwood 1967b and Green 1973a).

In the Canberra experiments the iron loss and the oxidation state of iron have been carefully monitored as standard practice in any project by direct microanalysis by spectrophotometric methods of the bulk samples after runs (Green & Ringwood 1967a,b; Kiss 1974). This can be done on 1-2 mg samples and it is surprising indeed that other laboratories have failed to apply this technology and persisted in experiments in which either both iron loss and oxidation state remain unmonitored or oxidation state is controlled (at unknown Fe^{3+} , Fe^{2+} values) using an external hydrogen buffer while iron loss remains undetermined. It has also long been known that the piston cylinder apparatus, using a graphite furnace and either talc, talc + boron nitride or talc + pyrex glass sleeves surrounding the graphite heater, produces high hydrogen fugacities and low oxygen fugacities within the Pt or Ag-Pd sample container. This was illustrated in the FeO , Fe_2O_3 data of Green & Ringwood (1967a,b, and later papers), particularly by Banno & Green (1968) in studies of the system diopside + albite + magnetite + quartz and by the Green & Sobolev (1975) demonstration of very low Fe_2O_3 content of ilmenites crystallized under a wide range of water contents. Nehru & Wyllie (1975) note determinations by a number of workers showing that using the single capsule method and the standard 'dry' or 'wet' furnace assemblies, oxygen

fugacities in the sample capsule are close to the NNO buffer and usually between the NNO and MW buffers. Experiments in our laboratory on stability of buffer assemblages confirms $f(\text{O}_2)$ conditions < NNO for our normal run procedures. Mysen & Boettcher (1975a,b) concur in this assessment and refer to their own experiments under these conditions as ' f_{H_2} (NNO)' (e.g. 1975b, p. 557, p. 577) or $f_{\text{H}_2} > \text{NNO}$. Curiously, they refer to experiments by Green, using the same type of furnace assembly, as 'unbuffered (f_{H_2})' (1975b, p. 554). In fact, in the experiments reported by Green (1973a,b) the charges were buffered by the furnace assembly, the oxidation state of iron was determined (cf. Table 1) and microprobe analyses of the bulk sample were carried out routinely for all major elements and reported simply as 100Mg/Mg + ΣFe ratios for the charges (Green 1973a, Tables 1-9). Only at 10 kbar, 1200°C (100Mg/Mg + $\Sigma\text{Fe} = 89.7$, initially 85.2), 10 kbar, 1100°C (100 Mg/Mg + Fe = 86.4) and 20 kbar, 1100°C (100 Mg/Mg + Fe = 85.7, initially 85.2) was there appreciable iron loss from the charge. These iron losses were much lower than those reported by Nehru & Wyllie (1975) and reflect the lower sample/metal capsule ratio and longer run times used by Nehru & Wyllie. These authors recognized their dilemma in that shorter run times resulted in failure of the crushed rock (- 200 mesh) to reach equilibrium and longer run times resulted in excessive iron loss. These problems were minimized in the Canberra work by the use of a sintered oxide mix (grain size < 5 microns, olivine + pyroxenes + plagioclase mineralogy) as starting material, larger sample/metal capsule ratios and empirically established run times, and the resultant charges were carefully checked for bulk composition by the methods noted above. These data refute the contention of Mysen & Boettcher (1975a,b) that no significance can be attached to changes

TABLE 1: SPECTROPHOTOMETRIC DETERMINATION OF FeO AND Fe_2O_3 IN SAMPLES AFTER HIGH-PRESSURE RUNS

Composition	%H ₂ O	Pressure (kbar)	Temp (°C)	Time (hrs)	Sample Capsule	Initial		Final	
						FeO	Fe ₂ O ₃	FeO	Fe ₂ O ₃
Pyrolite - 40% olivine	2	15	1000	24	Ag ₇₅ Pd ₂₅	8.1	0.5	8.2	0.3
Pyrolite - 40% olivine	10	15	1000	6.5	Ag ₇₅ Pd ₂₅	8.1	0.5	8.1	0.6
Pyrolite - 40% olivine	10	15	900	31	Ag ₇₅ Pd ₂₅	8.1	0.5	7.7	0.4
Glass 1	15	10	1180	0.5	Ag ₅₀ Pd ₅₀	7.9	0.6	5.8	1.0
Glass 1 + 3% O1	15	10	1180	0.5	Ag ₅₀ Pd ₅₀	7.9	0.6	5.5	0.9
Glass 3 + 2% O1	15	10	1080	0.5	Ag ₇₅ Pd ₂₅	6.8	0.5	5.5	1.1
Glass 3 + 1% CaO	15	10	1060	0.5	Ag ₇₅ Pd ₂₅	6.7	0.5	6.4	0.5
Glass 5 + 10% Opx	20	20	1100	0.25	Ag ₇₅ Pd ₂₅	8.9	0.5	8.0	0.5

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in $100 \text{ Mg/Mg} + \Sigma \text{ Fe}$ values of minerals and that there is no validity in the use of this ratio to test for equilibrium between quenched glass and olivine crystals (in experiments carried out at $f_{\text{O}_2} < \text{NNO buffer}$).

It is useful to comment on two further technical aspects of the experimental studies. Green (1973a) added 10 wt. % water to the (pyrolite-40% olivine) composition (Green & Ringwood 1967c) yielding experiments equivalent to (pyrolite + 6% water). The charges after the runs were coherent, and either 'rock-like' to 'coherent but readily crushable' — such samples are readily mounted and polished so that textures and crystal/melt/vapor relationships can be readily observed. Nehru & Wyllie (1975) used a partly serpentinized peridotite containing 5.7% water

and apparently obtained similar coherent charges (Nehru & Wyllie 1975, Fig. 2). However, in our recent experiments on lherzolite (-200 mesh) + 16-22% water (duplicating Mysen & Boettcher's 1975a,b sample mixes), the sample is recovered as an incoherent white powder, pouring cleanly from the capsule as a disaggregated mineral powder, most grains being coated with glass films quenched from the vapor phase and/or silicate melt. Textural relationships in this material are much more obscure and the high proportion of vapor phase results in appreciable composition change in the condensed phases (cf. the occurrence of forsterite in subsolidus assemblages of the enstatite+ H_2O system—Kushiro *et al.* 1968).

A second aspect of the experimental studies is the identification of quench borders on primary crystals. Green (1972) noted that 0.5 micron

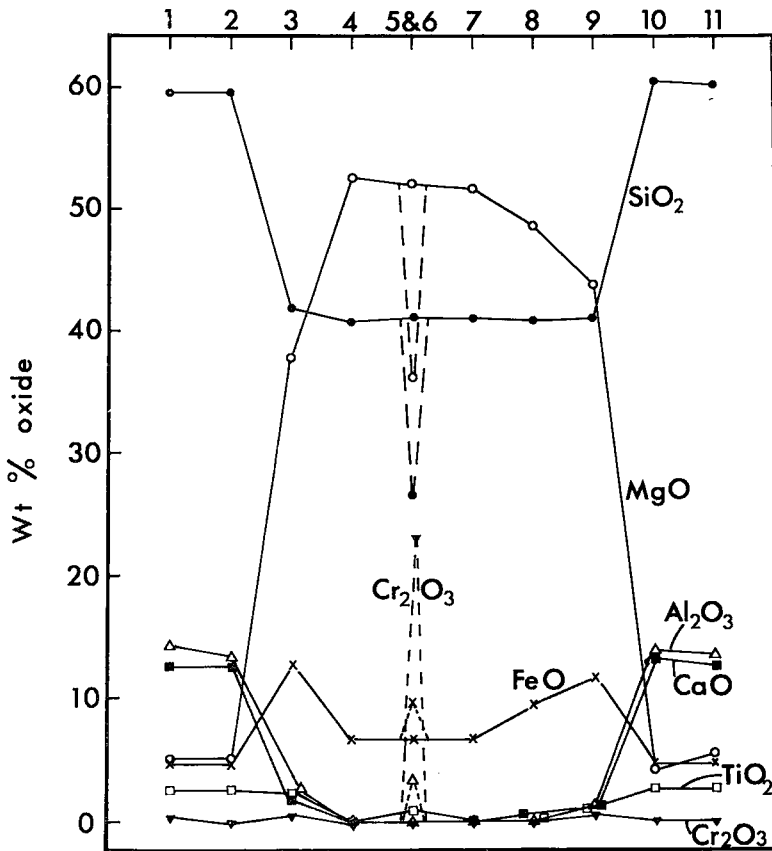


Fig. 1. Analytical data from (pyrolite - 40% olivine) composition at 10 kbar, 1200°C, 10% H_2O added, showing analyses of olivine crystals (4,5,7), typical analyses of glass areas free of olivine crystals (1,2,10,11), and three analyses at the edges of olivine crystals (3,8,9) showing iron enrichment and partial admixture of glass (<3% CaO , Al_2O_3 , >10% FeO). The analytical data from a tiny chromite grain (6) of 1-2 micron diameter and included in olivine are also shown.

quench borders on 10-micron olivine crystals result in >33% volume increase of crystallized olivines and Green (1973a) published an analysis of quench olivine ($FO_{84.5}$) outgrowth on primary olivine (FO_{92}). Nehru & Wyllie (1975) and Mysen & Boettcher (1975a,b) did not find such borders, suggesting that such borders are <2 micron (approx.) thick in their experiments. Raw analytical data for such a quench border outgrowth obtained by the TPD microprobe (<0.5 micron beam, energy dispersive analytical system; Reed & Ware 1973, 1975) are illustrated in Figure 1. The only grain boundary effect able to produce these variations in X-ray intensities is real iron enrichment at the grain boundary. "Correction" of the border analysis for glass admixture (calculated by assuming no CaO in the olivine border) and high TiO_2 yielded the olivine composition ($FO_{84.5}$) given by Green (1973a).

PREVIOUS EXPERIMENTAL TESTING OF EQUILIBRIUM MELT COMPOSITIONS

Experimental studies of simple systems are of great value in suggesting explanations of observed crystallization behavior of natural complex melts (e.g., the incongruent melting of enstatite at low pressures and the appearance of olivine phenocrysts and pigeonite reaction rims in quartz normative basalts) but are of qualitative value only for prediction of crystallization behavior in complex natural rock compositions. From studies of the enstatite+water system and then of related systems such as $Fo+Di+Qz+H_2O$ and $Fo+Ne+Qz+H_2O$, Kushiro (1970, and earlier papers) argued that water-saturated melting of peridotite would produce quartz-normative liquids at pressures to at least 25 kbar. Green (1970) took a natural quartz-normative tholeiite displaying the classical low-pressure olivine+liquid₁⇌subcalcic pyroxene + liquid₂ reaction relationship and showed that, at 22.5 kbar, $P(H_2O)=P(\text{total})$, this composition did not have olivine as the liquidus phase (as would be predicted if the Kushiro hypothesis applied to this natural rock composition). Addition of olivine crystals sufficient to make the bulk composition exactly silica-saturated (neither quartz nor olivine in the norm) resulted in solution of the olivine and clinopyroxene was again the liquidus phase. The data showed that a typical natural quartz tholeiite could not be a direct partial melt of a peridotitic source rock at 22.5 kbar, even under water-saturated conditions. This method of testing hypotheses of partial melting by establishing $P, T, \%H_2O$ conditions where a given magma has the same liquidus phases (of the same composition) as the residual phases of the postulated

source composition, is of general application and has been followed consistently in the formulation and testing of a petrogenetic grid for basaltic magmas (Green & Ringwood 1967a; Green 1970, 1971, 1972, 1973a,b,c; Brey & Green 1975) and for lunar magmas (Green *et al.* 1975, Longhi *et al.* 1974). Nicholls & Ringwood (1973) evaluated the pressure range over which quartz tholeiites, saturated tholeiite and olivine tholeiite crystallized olivine as their liquidus phase under water-saturated conditions, establishing that the silica-saturated tholeiite could be derived by partial melting of a peridotite source under water-saturated conditions up to pressures between 17 kbar and 20 kbar. Nicholls (1974) carried out similar studies on andesite and basaltic andesite compositions showing that olivine was a liquidus phase to 5 kbar (andesite) and 10-15 kbar (two basaltic andesite compositions) under water-saturated conditions. These studies demonstrated the great importance of water in expanding the liquidus role of olivine to higher pressures in hydrous silica-rich magma compositions as predicted by Kushiro *et al.* (1968). A similar but less marked effect was noted in highly undersaturated magmas (Green 1973c) but in these compositions a more genetically important effect is the appearance of orthopyroxene in addition to or replacing clinopyroxene as a near-liquidus phase accompanying olivine (Green 1970, p. 43; 1971, p. 725). The results of the experimental studies under water-saturated conditions on both the postulated source compositions and on natural magmatic liquids from andesite to olivine tholeiite, were synthesized into an internally consistent picture (Green 1973a,b; Nicholls & Ringwood 1974) in which it was shown that the most siliceous liquids derived by partial melting of pyrolite at 10 kbar were magnesian quartz tholeiites (~55% SiO_2) or basaltic andesites and at 20 kbar were magnesian olivine tholeiites (~49% SiO_2).

These conclusions were opposed by Mysen & Kushiro (1974), Boettcher (1975), and Mysen & Boettcher (1975a,b) who affirmed that their experimental methods were adequate to attain equilibrium, that the compositions of glasses obtained in their experimental runs were unmodified by quenching problems, and that such glass compositions were those of equilibrium liquids appropriate to the P, T conditions of their experiments. Nicholls & Ringwood (1973) synthesized a glass of composition matching that obtained by Kushiro *et al.* (1968) in melting of a lherzolite at 26 kbar, 1190°C, $P(H_2O)=P(\text{total})$ and showed that its water-saturated liquidus at 26 kbar was at 940°C, not 1190°C, and that clinopyroxene, not olivine, was the liquidus

phase. Mysen & Kushiro (1974) ignored the temperature discrepancy but argued that liquids derived from an olivine-bearing residue need not have olivine as a liquidus phase at the P , T conditions of melting if a reaction relationship existed between olivine and liquid. Mysen & Boettcher (1975b) (see also Mysen & Kushiro 1974) tested a glass from a much lower temperature partial melting run (940°C, at 15 kbar) and prepared a glass of the composition analyzed in the herzolite melting run (coexisting with olivine, orthopyroxene, clinopyroxene, amphibole and spinel). This glass did not crystallize olivine or amphibole as liquidus phases at 15 kbar although its liquidus temperature (>950°C) was close to that of the partial melting run and amphibole appeared between 950°C and 930°C. Furthermore, addition of 9.4% olivine to the supposedly olivine-saturated composition did not result in olivine crystallization. Mysen & Boettcher (1975b) considered that these results supported their conclusions on genesis of highly siliceous liquids and did not recognize that their data at 940°, 15 kbar were inconsistent with the detail of their model and also greatly aggravated the problems for their higher temperature, equally siliceous 'equilibrium liquids' (Mysen & Boettcher 1975b, Table 9).

NEW DATA ON WATER-SATURATED MELTING OF PYROLITE

The conclusions by Mysen & Boettcher (1975a) that their peridotite solidi were at temperatures <950°C prompted a careful examination of the pyrolite melting relations at 15 kbar to augment the previously published data at 10 kbar and 20 kbar (Green 1973a,b).^{*} Optical examination of crushed sample (mounted in refractive index oils) and of the polished surfaces of uncrushed samples showed a distinctive textural change between 970°C and 1000°C with runs at temperatures $\geq 1000^\circ\text{C}$ showing interstitial glass and quench phases. Analyses of coexisting minerals are given in Table 2 and plotted in terms of 100 Mg/Mg+ Σ Fe vs. temperature in Fig. 2. The disappearance of primary amphibole (acicular, feathery amphibole at higher temperatures is more siliceous and Fe-rich and is a quench phase, cf. Green 1973a Tables 4,5,8,9) and appearance of ilmenite between 1000°C and 1020°C coincides with a marked increase in

Mg/Mg+Fe value of olivine, orthopyroxene and clinopyroxene. These changes require the presence of a large melt fraction (>15%) at 1020°C. The consistency of Mg-value of orthopyroxene and olivine between 900°C and 970°C and the small increase in this value in both orthopyroxene and olivine (the most accurately analyzable phases) at 1000°C suggest that a small melt fraction is present at 1000°C. Unlike the 10 kbar data (Green 1973a) there is no distinctive change in Na/K ratio of amphibole between 970°C and 1000°C. The TiO₂-content of the amphibole increases with increasing temperature at constant pressure (Table 2) and decreases with increasing pressure at constant temperature (Table 2 and Green 1973a Tables 6,7,12). Ilmenite is a coexisting accessory phase at 20 kbar, probably also at 15 kbar and 10 kbar, but was only

TABLE 2. COMPOSITIONS OF MINERALS SYNTHESIZED IN (PYROLITE - 40% OLIVINE) COMPOSITION (GREEN 1973a TABLE 1) UNDER WATER-SATURATED CONDITIONS AT 15 KBAR

Temp. °C	WATER-SATURATED CONDITIONS AT 15 KBAR						
	900	930	950	970	1000	1020	1050
Time (hrs)	31	29	25	20	6	4	5
100 Mg/Mg+ Σ Fe _{olivine}	n.a.	83.9	83.8	83.3	84.2	85.7	86.4
	Amph	Amph	Amph	Amph	Amph	Ilm	
SiO ₂	46.7	46.3	45.7	46.0	44.5	1.0	
TiO ₂	1.1	1.2	1.4	1.5	1.7	54.9	
Al ₂ O ₃	12.1	11.5	12.0	11.8	13.2	0.5	
FeO	5.4	5.2	5.2	5.4	5.6	27.6	
MgO	19.2	19.0	18.3	18.5	18.7	12.9	
CaO	10.5	10.8	11.4	11.2	10.0	0.4	
Na ₂ O	1.8	1.9	2.1	2.05	2.1	-	
K ₂ O	0.45	0.5	0.6	0.5	0.5	-	
Cr ₂ O ₃	1.0	1.2	1.2	1.0	1.3	2.3	
100 Mg/Mg+ Σ Fe _{Amph}	86.3	86.7	86.3	85.9	85.7	45.4	
	Opx	Opx	Opx	Opx	Opx	Opx	Opx
SiO ₂	54.1	54.7	54.5	54.3	54.2	55.6	55.0
TiO ₂	0.3	0.3	0.3	0.4	0.4	0.3	0.3
Al ₂ O ₃	3.8	3.4	3.7	3.9	3.8	2.3	2.0
FeO	9.5	9.5	9.6	9.5	9.1	8.2	7.9
MgO	30.5	30.5	30.6	30.1	30.3	31.9	32.5
CaO	0.8	0.8	0.9	1.0	1.1	1.0	1.2
Cr ₂ O ₃	0.8	0.6	0.7	0.8	0.8	0.5	1.0
MnO	0.2	0.2	0.1	0.1	0.2	0.2	0.1
100 Mg/Mg+ Σ Fe _{Opx}	85.1	85.2	85.1	85.0	85.6	87.4	88.0
	Cpx	Cpx	Cpx	Cpx	Cpx	Cpx	Cpx
SiO ₂	53.6	53.0	52.1	52.5	53.5	53.1	
TiO ₂	0.7	0.5	0.7	0.7	0.8	0.4	
Al ₂ O ₃	3.3	3.2	4.0	4.3	3.1	2.6	
FeO	4.6	4.3	4.4	4.6	4.1	4.0	
MgO	16.5	17.4	17.2	17.1	17.6	18.0	
CaO	20.3	20.4	20.5	20.2	20.2	21.0	
Na ₂ O	0.3	0.3	0.3	-	0.1	-	
Cr ₂ O ₃	0.7	0.8	0.8	0.7	0.6	0.8	
100 Mg/Mg+ Σ Fe _{Cpx}	n.a.	86.4	87.8	87.4	86.8	88.4	88.9

*A new batch of (pyrolite-40% olivine) sintered mix was used with composition as given by Green (1973a Table 1) except that it contained 8.1% FeO and 0.5% Fe₂O₃.

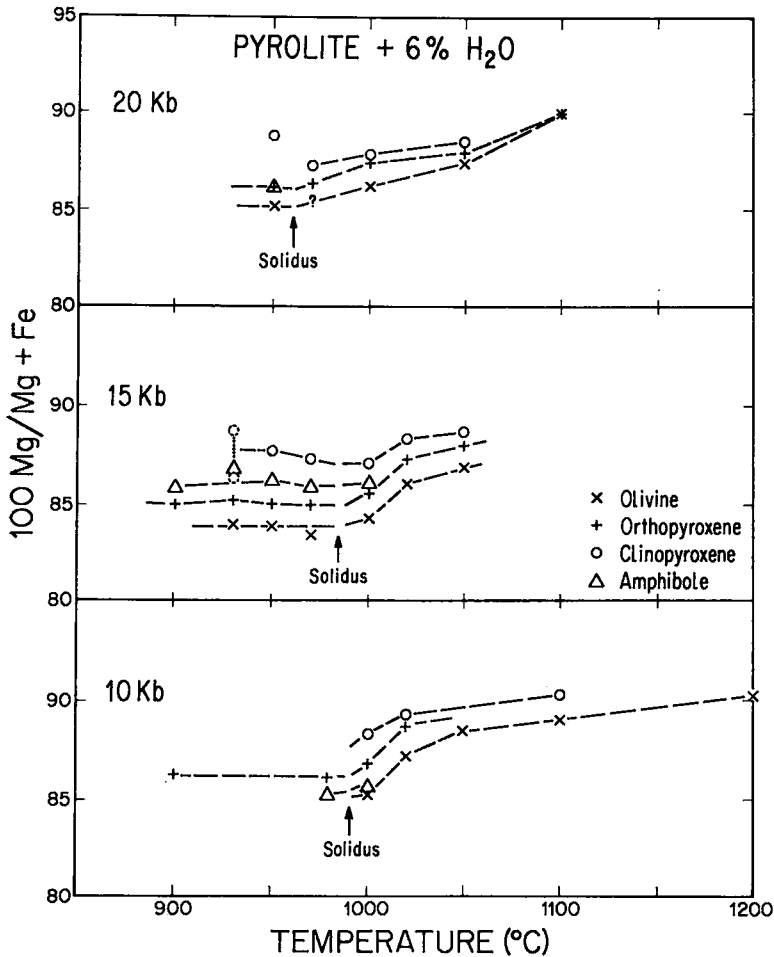


Fig. 2. Plot of temperature versus $100 \text{ Mg/Mg} + \Sigma \text{Fe}$ for minerals analyzed from (pyrolite - 40% olivine) + 10% H_2O at 10 kbar and 20 kbar (Green 1973a) and at 15 kbar (Table 2, this paper). The position of the solidus is shown at each pressure, as deduced from optical and mineral composition data.

sufficiently large and analyzable above the amphibole breakdown at 15 kbar and 20 kbar.

In view of the discussions by Mysen & Boettcher (1975a,b) on $f(\text{H}_2)$, $f(\text{O}_2)$ and oxidation state it is important to note that the analyses of the charges after experiments show little or no iron loss and very high $\text{FeO}/\text{Fe}_2\text{O}_3$ ratios (Table 1). This is confirmed by the ilmenite analyses (Table 2; Green 1973 Table 10) which demonstrate little or no Fe_2O_3 solid solution and are compatible with real mantle conditions (Green & Sobolev 1975). Note also that the differences in $100 \text{ Mg/Mg} + \Sigma \text{Fe}$ values of coexisting amphiboles, olivine and clinopyroxenes (Fig. 2) when compared with data from natural assemblages in which Fe^{3+} and Fe^{2+} are separately determined

(Frey & Green 1974) show that there is little or no Fe^{3+} in amphibole in the 15 kbar runs, and probably small Fe^{3+} contents in the 10 kbar and 20 kbar amphiboles (shorter run times in the 10 kbar, 20 kbar runs, starting mix with 0.8% Fe_2O_3 , compared with 0.5% Fe_2O_3 for the 15 kbar runs). The new experimental data confirm that the water-saturated solidus for pyrolite lies between 970°C and 1000°C at 15 kbar, consistent with the interpolation from the previous 10 kbar and 20 kbar data. The upper limit of amphibole stability lies between 1000°C and 1020°C at 15 kbar, slightly higher than interpolated from the 10 kbar and 20 kbar data. The new data give no support to Mysen & Boettcher's (1975a,b) contention that solidi of their perido-

tites, in some cases of more refractory compositions than (pyrolite - 40% olivine) composition, lie at or below 900°C. I consider that these latter solidi were incorrectly determined, errors being caused by lack of equilibrium in the coarsely crystalline starting mixtures and the difficulty of distinguishing vapor-phase quench from silicate-melt quench particularly in bulk compositions where the proportion of vapor phase is high and extremely high in relation to the small proportion of reactive silicate solid phases in a coarse-grained mineral mixture.

EXPERIMENTAL TESTING OF CALCULATED EQUILIBRIUM PARTIAL MELTS OF PYROLITE

Previous sections reviewed the evidence against acceptance of silicate glass compositions (anal-

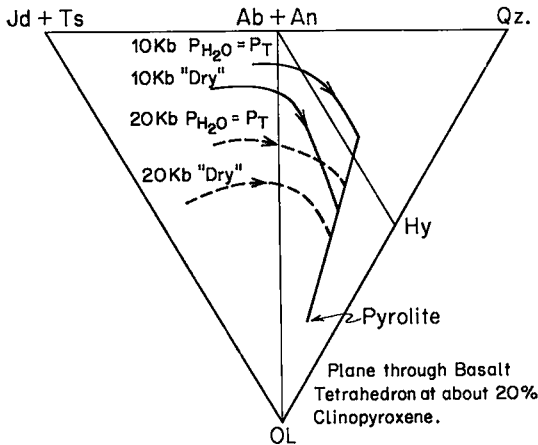


FIG. 3. Schematic diagram illustrating the partial melting trend (i.e. trace of liquid compositions with increasing degrees of melting) of pyrolite at 10 kbar and 20 kbar. The "dry" curves refer to melting paths for pyrolite + 0.1% H₂O approximately (Green 1970, 1971, 1973a). The P_{H₂O} = P_T paths refer to water-saturated melting. The low-temperature parts of the curves are cotectic melting paths in which olivine and one or two pyroxenes are residual phases and the beginning of melting involves at least olivine, two pyroxenes, amphibole and spinel. The compositions of residual pyroxenes are of course quite different in the 'dry' and P_{H₂O} = P_T cases. For higher degrees of melting, olivine alone is the residual phase. The different compositions at which the partial melting trends intersect the olivine control line are determined by the data in this paper and in Green (1973a, 1970, 1971) and Green & Ringwood (1967b). Note the relevance of behavior in the simple system Fo-Qz (Kushiro *et al.* 1969) in which water-saturated melting of olivine + enstatite assemblages produces a quartz-normative liquid at 20 kbar, and the simple system Ne-Fo-Qz (Kushiro 1972) in which the water-saturated beginning of melting lies in the nepheline-normative field.

TABLE 3. CALCULATED EQUILIBRIUM LIQUIDS FROM WATER-SATURATED MELTING OF PYROLITE (GREEN 1973a) AND PREFERRED COMPOSITIONS AFTER EXPERIMENTAL TESTING

	10 kbar, 1200°C		10 kbar, 1100°C		20 kbar, 1100°C	
	1	2	3	4	5	6
SiO ₂	54.6	53.8	56.1	55.5	49.4	49.8
TiO ₂	2.2	2.0	2.5	2.5	2.7	2.6
Al ₂ O ₃	10.7	9.7	12.4	12.3	12.5	12.0
Fe ₂ O ₃	1.5(0.6)*	0.3	1.7(0.5)*	0.5	0.5(0.5)*	0.5
FeO	6.9(7.9)*	9.1	5.8(6.9)*	6.8	8.9(8.9)*	9.0
MnO	0.2	0.2	0.1	0.1	0.2	0.2
MgO	11.9	14.1	9.3	9.3	11.5	12.6
CaO	9.4	8.6	9.5	10.4	10.9	10.4
Na ₂ O	1.9	1.7	2.0	2.0	2.1	2.0
K ₂ O	0.4	0.4	0.5	0.5	0.5	0.5
Cr ₂ O ₃	0.1	0.1	0.1	0.1	0.2	0.2
Qz	6.3	3.0	11.1	8.5	-	-
Or	2.4	2.4	3.0	3.0	3.0	3.0
Ab	16.1	14.4	16.9	16.9	17.9	17.0
An	19.5	18.0	23.4	23.1	23.3	22.3
Di	21.7	19.6	18.9	22.9	25.0	23.6
Hy	27.5	38.2	19.4	20.2	14.5	18.0
Ol	-	-	-	-	10.1	10.2
Chr	0.2	0.2	0.2	0.2	0.3	0.3
Ilm	4.2	3.8	4.7	4.8	5.2	5.0
Mt	2.2	0.4	2.6	0.7	0.7	0.7
100 Mg Mg+Fe ²⁺	73	73.5	70.5	70.5	70	71.5

* FeO, Fe₂O₃ as analyzed on initial glasses (E. Kiss, analyst).

alyzed from partial melting runs on peridotite compositions) as equilibrium liquids due to the problems caused by quench outgrowth of primary crystals and the appearance of quench clinopyroxene, amphibole, and possibly chlorite. Green (1973a) used knowledge of the bulk composition of the charge (before and after runs), the composition of mineral phases present, the relative proportions of mineral phases where more than one was present, and the empirical partition coefficient (Fe/Mg)_{ol}/(Fe/Mg)_{liquid} = 0.3 (Roeder & Emslie 1971) to calculate equilibrium partial melts at 10 kbar, 1200°C; 10 kbar 1100°C; and 20 kbar, 1100°C. These liquids were considerably less siliceous than the analyzed glasses at the appropriate P, T conditions and were used to outline a petrogenetic grid for water-saturated melting of pyrolite (Green 1973a; Fig. 3). This work concluded that the most silica-saturated liquids obtainable by partial melting of pyrolite at 20 kbar, water-saturated conditions, were olivine-poor tholeiites (<10% normative olivine).

If this method of derivation of melt compositions is to earn more credence than the discredited method discussed previously then it is obviously necessary to test these calculated melts in the same manner outlined previously. Thus if the calculated equilibrium melt from the 20 kbar, 1100°C run is indeed a partial melt from pyrolite, its water-saturated liquidus should

lie at 20 kbar, 1100°C and olivine and orthopyroxene should either be the liquidus phases or become liquidus phases after addition of <5% (approx.) of either phase. Similar strictures apply to the 10 kbar calculated liquid compositions.

The compositions tested experimentally are listed in Table 3, columns 1, 3 and 5. These compositions were prepared as glasses and the actual analyzed contents of FeO and Fe₂O₃ are listed in Table 3. The iron loss to AgPd capsules is small (Table 1) but, as is anticipated, greater than that in the largely crystalline (pyrolite - 40% olivine) compositions at lower temperature and longer run times (Table 1). Experimental data for these compositions are given in Table 4.

10 kbar, 1200°C

The calculated equilibrium liquid for 10 kbar, 1200°C was found to crystallize olivine as the liquidus phase, as predicted, but at $T < 1200^\circ\text{C}$, probably at 1160-1170°C (there is some uncertainty due to optical identification of olivine in the crushed mounts of some runs but its absence in that part of the sample mounted for electron probe analysis). Addition of 3%, 5% and 10% olivine (Fo₉₀) crystals showed that ~10% olivine must be added before rare, euhedral olivine (Fo₉₀₋₉₁) persisted as the liquidus phase at 1180°C. From these data it is inferred that the initial, calculated equilibrium liquid was slightly too siliceous and high in normative quartz and the more olivine-rich composition listed in Table 3 column 2 is thus preferred. Column 2 lists the estimate of the liquid derived by ~35% equilibrium partial melting of pyrolite at 10 kbar, 1200°C, water-saturated conditions leaving residual olivine (Fo₉₀) and a trace of chrome spinel. This equilibrium partial melt composition should be contrasted with the analyzed glass compositions (Green 1973a, Table 2 column 6, 7) demonstrating the strong effects of quench crystallization.

10 kbar, 1100°C

The calculated equilibrium liquid (glass 3) for 10 kbar, 1100°C was found to crystallize enstatite and diopside (Table 4) at 10 kbar, 1080°C and to be above its liquidus temperature at 1100°C. For the pyrolite-40% olivine composition at 10 kbar, 1100°C the residual phases were olivine (Mg₉₀) and clinopyroxene (Mg₉₀). Addition of 5% olivine to glass 3 yielded olivine (Mg₉₀) and orthopyroxene (Mg₉₀) as near-liquidus phases at 1100°C and addition of 1% CaO to glass 3 yielded clinopyroxene (Mg₉₀) alone as near-

TABLE 4. DETAILS OF EXPERIMENTAL RUNS ON CALCULATED EQUILIBRIUM MELT COMPOSITIONS (GREEN 1973a) AND ON VARIANTS MADE BY ADDING SMALL QUANTITIES OF OLIVINE, ORTHOPYROXENE AND CaO.

Composition ⁺	Run No.	Pressure (kbar)	Temp (°C)	Time (mins)	Products (observed in polished mount).
1	4406	10	1200	30	Quench (above liquidus)
1	4418	10	1180	30	Quench (very rare olivine seen in crush)
1	4488	10	1180	30	Quench
1	4497	10	1170	30	Quench (very rare olivine seen in crush).
1 + 3% O1*	4501	10	1180	30	Quench
1 + 3% O1	4503	10	1160	30	Quench
1 + 5% O1	4507	10	1180	30	Quench
1 + 5% O1	4515	10	1160	15	Quench
1 + 5% O1	4518	10	1150	15	O1 ₉₀ +Quench
1 + 5% O1	4508	10	1140	30	O1 ₈₈₋₉₂ +Quench
1 + 10% O1	4540	10	1180	15	O1 ₉₀₋₉₁ +Quench
3	4410	10	1100	30	Quench
3	4412	10	1080	30	Op ₈₈ +Cpx ₈₈
3 + 2% O1	4506	10	1120	30	Quench
3 + 2% O1	4509	10	1110	30	Op ₈₉ +Quench
3 + 2% O1	4504	10	1100	30	Op ₉₁ +Quench
3 + 5% O1	4519	10	1120	15	Quench
3 + 5% O1*	4524	10	1100	15	O1 ₈₆₋₈₈ +Op ₈₉₋₉₀ +Quench
3 + 1% CaO*	4525	10	1100	15	Cpx ₈₉ +Quench
3 + 1% CaO	4534	10	1080	15	Cpx ₈₇₋₈₈ +Quench
3 + 1% CaO	4547 4550	10	1060	30	Op ₈₅ +Cpx ₈₆ +Quench
5	4541	20	1120	15	Cpx _{88.5} +Quench
5	4535	20	1110	35	Cpx _{88.5} +Quench
5	4408	20	1100	60	Cpx ₈₈ +Quench
5	4417	20	1080	60	O1 ₈₅ +Cpx ₈₇ +Quench
5	4419	20	1060	60	O1 ₈₂ +Cpx ₈₆ +Quench
5 + 5% Enst.*	4552	20	1110	20	O1 ₈₅₋₈₆ +Cpx ₈₈ +Quench
5 + 5% Enst.	4546	20	1100	20	O1 ₈₆ +Cpx ₈₈ +Quench
5 + 5% Enst.	4551	20	1080	20	Op ₈₄₋₈₅ +Cpx ₈₆ +Quench
5 + 5% Enst.	4559	20	1080	20	O1 ₈₃₋₈₄ +Cpx ₈₇ +Quench
5 + 10% Enst.	4572	20	1140	15	Quench
5 + 10% Enst.	4571	20	1130	15	Op ₈₆ +Cpx ₈₇ +Quench
5 + 10% Enst.	4568	20	1120	15	Op ₈₅₋₈₆ +Cpx ₈₆₋₈₈ +Quench
5 + 10% Enst.	4564	20	1100	15	O1 ₈₆ +Op ₈₆₋₈₈ +Cpx ₈₈ +Quench
5 + 10% Enst.	4563	20	1100	15	Op ₈₅ +Cpx ₈₆ +Quench

⁺See Table 3

*Olivine added was finely ground (<20µm) olivine from Iherzolite 2604 (Frey & Green 1974) of composition Mg₉₃. Enstatite added was finely ground (<10x30µm laths) enstatite from enstatite eclogite (Green 1969) and was of composition Mg₉₅, 0.9% Al₂O₃, 0.5% CaO. CaO was added as Analar CaCO₃ so that in fact these runs contained 0.9 wt.% CO₂ in addition to 15 wt.% H₂O.

All runs at 10 kbar contained 15 wt.% H₂O, those at 20 kbar contained 20 wt.% H₂O. At 10 kbar, experiments at <1100°C were carried out in Ag₉₅Pd₅ capsules, those at >1100°C used Ag₅₀Pd₅₀ capsules. At 20 kbar all experiments were carried out in Ag₇₅Pd₂₅ capsules.

For Run No. 4564, read 1110°C.

liquidus phase at 10 kbar, 1100°C. It is clear that glass 3 is compositionally extremely close to a liquid which has its 10 kbar, water-saturated liquidus at 1100°C and which is saturated by olivine, orthopyroxene and clinopyroxene at that temperature. It is particularly notable that the clinopyroxene crystallized as the near-liquidus phases from glass 3 (and modified glass 3) compositions at 10 kbar, ~1100°C, is compositionally identical within analytical error with that of the residual clinopyroxene at 10 kbar, 1100°C in

TABLE 5: COMPOSITIONS OF LIQUIDUS AND NEAR-LIQUIDUS PHASES OF LIQUIDS OF TABLE 3. COMPARE WITH RESIDUAL PHASES AT SIMILAR P, T . FOR PYROLITE - 40% OLIVINE (GREEN 1973a).

	Glass 3		Glass 3 + 5% Ol		Glass 3 + 1% CaO			Glass 5		Glass 5 + 5% Enst.		Glass 5 + 10% Enst.				
	10 kbar, 1080°C		10 kbar, 1100°C		10 kbar, 1100°C			20 kbar, 1120°C		20 kbar, 1080°C		20 kbar, 1100°C		20 kbar, 1110°C		
	Opx	Cpx	Ol	Opx	Cpx	Q-Cpx	Q-Cpx	Cpx	Ol	Cpx	Ol	Cpx	Ol	Opx	Cpx	Q-Amph
SiO ₂	56.9	54.5	41.0	54.4	54.3	53.9	48.8	53.5	40.9	53.8	40.5	53.3	40.2	56.7	54.6	44.9
TiO ₂	0.2	0.4	-	0.2	0.3	0.6	4.0	0.4	-	0.4	-	0.4	-	0.2	0.2	2.9
Al ₂ O ₃	0.4	1.0	-	0.6	1.0	1.7	6.8	1.3	-	2.0	-	2.1	-	1.2	1.6	11.0
FeO	8.0	4.3	11.1	6.6	4.1	5.6	7.6	4.1	14.4	4.5	12.7	4.1	13.3	8.1	4.2	9.9
MnO	-	-	-	-	-	-	-	-	0.1	-	0.1	-	-	0.1	-	-
MgO	32.3	18.7	47.7	33.0	18.5	18.5	15.6	17.9	45.5	17.8	46.3	17.3	46.4	31.9	18.1	15.9
CaO	1.9	20.2	0.2	1.6	20.8	18.9	16.9	21.4	0.4	20.5	0.1	20.9	0.1	1.3	20.1	9.7
Na ₂ O	-	-	-	-	-	-	0.2	-	-	0.1	-	-	-	-	-	1.7
Cr ₂ O ₃	0.4	0.9	-	-	1.0	0.8	0.1	1.4	-	1.0	0.1	1.8	-	0.5	1.1	.2
	87.8	88.5	88.4	89.9	89.0	85.5	78.4	88.6	84.9	87.5	86.5	88.2	86.1	87.6	88.5	74.2

(pyrolite-40% olivine + 10% H₂O; Green 1973a). In the (pyrolite-40% olivine) composition, orthopyroxene was not present in the polished mount but rare grains were identified optically in the crushed portion of the charge and the abundance of orthopyroxene at 10 kbar, 1050°C suggests that 10 kbar, 1100°C is very close to the temperature of disappearance of orthopyroxene as a residual phase in water-saturated melting of pyrolite. As Mysen & Kushiro (1974) have pointed out, if olivine and quartz-normative liquid are in a reaction relationship (to precipitate orthopyroxene at lower temperature) under water-saturated conditions at 10 kbar, then the liquid separated from an olivine-bearing residue may have orthopyroxene, not olivine as its liquidus phase. However addition of olivine to that liquid must result in persistence of olivine, either in place of or additional to orthopyroxene. These are precisely the relationships observed in the glass 3 composition and its modifications by CaO and olivine addition.

20 kbar, 1100°C

The calculated equilibrium liquid (glass 5) at 20 kbar, 1100°C has clinopyroxene as its liquidus phase at 1120°C, with olivine appearing between 1100°C and 1080°C. Addition of 5% enstatite crystals resulted in solution of enstatite and precipitation of olivine and clinopyroxene as liquidus phases, but addition of 10% enstatite resulted in persistence of some cores of relict enstatite (low Al, low Ca) and reaction of rims and smaller crystals to more Mg-rich, aluminous and calcic enstatites (cf. Table 4 footnote, and Table 5) and coprecipitation of clinopyroxene (1130°C, 1120°C) or clinopyroxene and olivine

(1110°C). Compositions of liquidus pyroxenes in the glass 5 and related compositions are again very close to the residual pyroxenes in (pyrolite-40% olivine) at 20 kbar, 1100°C (orthopyroxene, possible primary clinopyroxene cores to quench clinopyroxene; see Green 1973a Table 8) and 20 kbar, 1050°C (orthopyroxene and clinopyroxene). This compositional similarity shows that the Al₂O₃, TiO₂, Na₂O, and Mg-values, as well as the normative composition, of the calculated equilibrium liquid are about right for the liquid in equilibrium with the observed residual pyrolite mineralogy. Column 6, Table 3 lists the preferred composition, slightly richer in enstatite and lower in diopside content than glass 5, which has the correct liquidus phases of the correct composition to be a water-saturated partial melt from pyrolite at 20 kbar, 1100±20°C. Note that the difference from the original calculated liquid (glass 5) implies that the roughly estimated ratio of 3:2 for residual olivine:orthopyroxene in the original partial melting run (Green 1973a Table 8) was too low, and a 5:3 ratio would have been better. The 'reversed' partial melting experiments confirm that equilibrium partial melting of pyrolite under water-saturated conditions at 20 kbar, 1100°C will produce 27±1% melt of magnesian olivine tholeiite composition (~10% normative olivine, ~18% normative hypersthene and having SiO₂ content of ~50%) leaving residual olivine, orthopyroxene and possibly minor clinopyroxene. The contrast between this equilibrium melt and the highly siliceous quenched glass compositions (with their water-saturated liquids at 950°C-1000°C) obtained at 20 kbar, 1100°C accentuates the quenching problem in partial melting experiments. Even in above-liquidus and near-liquidus runs, the water-saturated basaltic liquids

did not quench to clear glass but grew quench outgrowths on primary phases (Table 4) and nucleated fibrous or acicular amphibole and (?)mica or chlorite laths during quenching. The problem is aggravated when such basaltic liquids are interstitial to common crystals which grow during quenching and act as nucleation sites for quench phases.

CONCLUSIONS

The data presented in this paper, when combined with the previously published data on the partial melting relationships of pyrolite under water-saturated conditions (Green 1973a,b) define the compositions of liquids formed by saturated melting of pyrolite at 10 kbar, 1100°C and 1200°C, and 20 kbar, 1100°C. It has been shown that, provided the bulk composition of the peridotite charge is known, (iron loss is monitored and oxygen fugacity maintained <NNO buffer), the mineral compositions analyzed, and the relative proportions of minerals estimated, then it is possible to use this information together with known equilibrium crystal/liquid partition relationships to calculate equilibrium liquid compositions (Green 1973a). It is then possible to test and confirm the reliability and accuracy of the calculated liquids by running these compositions at the appropriate *P*, *T*, *P*(H₂O) conditions to confirm that their liquidus temperatures and liquidus phases match those of the residual peridotite. This general approach to establishing a petrogenetic grid for mantle magma genesis has now been demonstrated for dry melting (Green & Ringwood 1967b,c), water-undersaturated melting (Green 1970, 1971, 1973c), and water-saturated melting. In the first two cases, it was possible to use petrological and geological arguments to identify the natural mantle-derived liquids and to use these compositions as the basis for the petrogenetic studies. In the latter case, although it has often been suggested that the distinctive basaltic and andesitic magmas of island arcs are the products of water-saturated melting of the upper mantle, it has not been possible (in the absence of transported high-pressure xenoliths) to objectively identify mantle-derived, unfractionated liquids in the island arc environment. The investigation of water-saturated melting of pyrolite is thus more completely an empirical, experimental exercise with the complementary aspects of partial melting experiments on peridotite and liquidus studies on potential melt products as presented in this paper.

The data presented by Green (1973a,b) and in this paper show that at 10 kbar, 1100°C, under

water-saturated conditions, the pyrolite composition will contain 28±1% liquid with a composition classifiable as a magnesian quartz tholeiite or magnesian basaltic andesite composition (Table 3, columns 3, 4). With increasing degrees of melting, clinopyroxene and olivine enter the melt until at 10 kbar, 1200°C the pyrolite is 35±1% molten and the liquid is a magnesian quartz tholeiite (Table 3, column 2). Higher degrees of melting, dissolving further olivine, will produce olivine-poor tholeiitic liquids with very low Al₂O₃, CaO, Na₂O contents. The compositions of liquids nearer the pyrolite solidus cannot as yet be uniquely determined since calculation of such liquids would require knowledge of the relative proportions of olivine, pyroxenes and amphibole (at 1000°C) among the residual crystals. However, the increasing modal abundance of orthopyroxene and clinopyroxene, the reaction relationship between olivine and liquid to precipitate pyroxene, and the strong partitioning of Na, K, Ti into the liquid relative to pyroxenes and olivine, show that liquids at <1100°C, 10 kbar are unlikely to have >55% SiO₂ and will decrease in SiO₂ and increase in Na₂O + K₂O towards the solidus. Unpublished data on partitioning of Na₂O and K₂O between amphibole and liquid between 10 kbar and 20 kbar, 1000°C to 1150°C shows that (Na₂O)_{liquid}/(Na₂O)_{amphibole} ≈ 2 and (K₂O)_{liquid}/(K₂O)_{amphibole} > 2. Thus the amphibole present at 1000°C, 10 kbar (Green 1973a) can be used to predict that the coexisting equilibrium liquid contains 4% Na₂O (approx.) and >0.6% K₂O — such liquids, with 50-55% SiO₂ and >14% Al₂O₃ would be olivine-normative and possibly nepheline-normative. The experimental studies show that the most silica-oversaturated liquids which can be derived from water-saturated partial melting of pyrolite at 10 kbar (30-40 km depth) are magnesian quartz-rich tholeiites with <10% normative quartz (Fig. 3). There is no temperature at which andesites with >55% SiO₂, >10% normative quartz, can be derived as equilibrium partial melting products of pyrolite at >10 kbar. The evidence herein and previously published (Green 1973a) on the problems of quenching of hydrous liquids show that analyses of siliceous glasses present in experimental runs do not represent equilibrium liquids even at 10 kbar, and cannot be used as evidence of the nature of magmas derived by water-saturated melting of peridotitic compositions.

At 20 kbar, 1100°C, the pyrolite composition contains 27 ± 1% melt under conditions of $P_{H_2O} = P_{Total}$ and the melt is of magnesian olivine tholeiite composition. Lower degrees of melting increase the importance of residual

pyroxenes but Na_2O , K_2O and TiO_2 remain strongly partitioned into the melt phase so that liquids are deduced to be more undersaturated and would probably become nepheline-normative between 1050°C and 1000°C . The presence of residual ilmenite at 1000°C and 970°C shows that the TiO_2 concentration in the liquid at these temperatures is sufficient to precipitate ilmenite — further data are required but unpublished experiments on basanite and mugearite composition (Irving & Green, unpublished) and on potassic mafurite composition (Edgar *et al.* in press) show that the TiO_2 content of such a liquid will exceed 3% TiO_2 . Partition coefficients for $(\text{Na}_2\text{O})_{\text{opz}}/(\text{Na}_2\text{O})_{\text{liquid}}$ suggest that the liquid at 20 kbar, 1100°C would contain $> 3.0\%$ Na_2O . At temperatures $> 1200^\circ\text{C}$ at 20 kbar, liquids may become slightly richer in SiO_2 and lower in normative olivine, up to the temperature at which orthopyroxene is no longer a residual phase ($1200\text{--}1250^\circ\text{C}$ approx.). Such liquids will be of magnesian, olivine-poor tholeiite composition. Quartz tholeiites, basaltic andesites, andesites or more siliceous liquids cannot be equilibrium partial melts from pyrolite under any conditions at pressures > 20 kbar.

SOURCE-PERIDOTITE GEOCHEMISTRY IN ISLAND ARC ENVIRONMENTS

It has previously been suggested (Green 1973a, p. 42) that some of the distinctive geochemical characteristics of magmas in the island arc environment may arise because the source peridotite producing the parental olivine-poor tholeiites to quartz tholeiite magmas (island arc tholeiitic series) is not of pyrolite composition but is of partly-depleted pyrolite composition. This 'depleted pyrolite' is envisaged as having lost a basaltic melt fraction ($< 10\%$ melt) in an earlier mid-ocean ridge or 'Hawaiian' type of magmatism and lithosphere formation. The 'depleted pyrolite', having lost a magmatic component under conditions of water-undersaturated melting, is mobilized as a source for further magmatism by access of water from subducted oceanic crust and lithosphere in the island arc environment, leading to conditions of water-saturated or near-saturated melting. An additional factor which must be considered in the geochemistry of island arc magmatism is the possibility that significant compositional change to peridotite overlying the Benioff zone is effected either by components transported through a vapor phase or by addition of a small water-saturated melt fraction from the subducted

oceanic crust (Ringwood & Green 1966; Green & Ringwood 1968; T. H. Green 1972; Nicholls & Ringwood 1973; Ringwood 1974). These factors emphasize that it is probably incorrect to consider the model pyrolite composition as the likely source composition for island arc magmatism. However the experimental study of pyrolite and the information on residual peridotite mineralogy permit inferences on the effects of variation in a source peridotite composition on the nature of the melting products.

If the source peridotite in island arc regions is depleted from pyrolite by the earlier loss of a basaltic fraction, then the K_2O , TiO_2 , Na_2O contents (and geochemically related trace elements Sr, Ba, Rb, REE, Zr, etc.) will be strongly depleted whereas SiO_2 , MgO, FeO, Al_2O_3 and CaO would have suffered less relative change. Water-saturated melting of such source material (still with subsolidus mineralogy of olivine, pyroxenes, amphibole, spinel) will produce a lower proportion of liquid than is present in pyrolite at a particular near-solidus temperature because of depletion of the low-melting fraction. At higher temperatures the liquids will be similar to those from pyrolite at the same T , P , % H_2O in terms of SiO_2 , MgO, FeO, CaO, Al_2O_3 contents but will be distinctly lower in Na/Ca, K/Ca, TiO_2 , REE etc. It is suggested that three of the most important characteristics of some island arc magma series are indicative of, or at least consistent with, such a depleted source region. Thus the low TiO_2 content characteristic of island arc basalts, in comparison with basalts from oceanic or stable continental environments, cannot be attributed to the presence of a relatively TiO_2 -enriched phase (amphibole, ilmenite, phlogopite) in equilibrium with a TiO_2 -poor liquid but would be a characteristic of a partly-depleted source region. Secondly, a most distinctive characteristic of many, but not all, island arc basalt-andesite-dacite series is the extremely calcic nature of phenocryst plagioclase (Whitford 1975). Basalts of such series may contain plagioclase phenocrysts up to An_{68} whereas the most calcic plagioclases crystallizing from basalts of oceanic or stable crust environments are An_{85} . It is suggested that parental magmas to those crystallizing plagioclase $> \text{An}_{60}$ are derived from source peridotites with much lower Na/Ca ratio than that of pyrolite. A third characteristic of some island arc magmas series is the low abundance of the REE and the relative LREE-depletion — this is consistent with a source peridotite which has previously lost a small, incompatible element-enriched basaltic fraction.

It may be inferred from the experimental studies of eclogite-facies melting (Green & Ring-

wood 1968; T. H. Green 1972) and from studies of natural pegmatites associated with eclogite in high-pressure metamorphic terranes (Green & Mysen 1972) that small degrees of melting of subducted eclogitic crust will yield silicic magmas of high K/Na ratio. The variation of K_2O contents, occurrence of basalt and andesites with $^{87}Sr/^{86}Sr > 0.703$ and with LREE-enriched characteristics, may primarily be due to variable proportions of added low-temperature melt fraction from subducted oceanic crust (cf. Ringwood 1974). Alternatively, variations in these incompatible-element abundances and related isotopic variations may reflect prior differences in source-peridotite composition. Frey & Green (1974) have shown that lherzolites from the upper lithosphere show at least two stages of development — an initial stage (A) of formation as residual lherzolite from a partial melting event, and a second stage (or stages; B) of variable and local enrichment in incompatible trace elements through either an added small melt fraction (olivine melilitite nephelinite) or migration through a H_2O -rich vapor phase. Differences in incompatible-element contents in parental island arc magmas may thus reflect differences in the extent to which stage(s) B have modified the lithosphere composition, e.g. if older crust/lithosphere regions are reactivated then resultant orogenic or island arc magmas are incompatible-element enriched and may have high $^{87}Sr/^{86}Sr$ ratios. In contrast, if younger crust/lithosphere regions, particularly of oceanic crust, are reactivated then the source peridotite and resultant magmas would be depleted in incompatible-element contents, have low Na/Ca ratios, etc. The purpose of the preceding discussion is to indicate the type of geochemical complexity which might be expected in the island arc situation — the geochemical 'fingerprints' of such complexity of the source region act as overprints of fine detail on parental magma compositions defined in the present experimental study. The experimental partial melting and crystallization studies, with their emphasis on the mineral phases and major-element compositions of liquids and crystals, are adequate to define the prime characteristics (e.g. andesite or basalt, olivine-normative or quartz-normative, high Al or low Al) of peridotite-derived liquids under water-saturated conditions but do not constrain trace elements, particularly incompatible trace elements. It has been conclusively demonstrated that the melting products of peridotitic mantle, at depths of magma segregation of >30 km, are basaltic (in the broad sense) and andesites, dacites or rhyodacites are not possible products of direct partial melting of peridotitic mantle. As dis-

cussed in earlier papers, the parental water-rich basalt magmas in the island arc situation will necessarily partly crystallize, and most commonly fractionate, by extraction of olivine, pyroxene, amphibole, plagioclase and titanomagnetite as they move toward the surface, yielding derivative, silica-enriched andesites, dacites, etc.

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