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# Mantle-derived magmas—roles of variable source peridotite and variable C–H–O fluid compositions

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**Abstract**—The system forsterite–nepheline–quartz is a useful simple system analogue of melting relations in upper mantle peridotite. The liquidus phase fields at 28 kbar differ from those at low pressure by expansion of the enstatite field at the expense of forsterite. The system illustrates a large field of liquid compositions, from model basanites to model quartz tholeiites, which can be derived from one peridotite source. More refractory source compositions permit a greater compositional range of derivative liquid compositions than more fertile compositions and in particular are required as source or parent compositions for enstatite-rich liquids.

The effects of C–H–O volatiles on melting relationships have been explored with $H_2O$, $CH_4$ and $CO_2$–vapour saturated experiments. The effect of water is to expand the olivine field and depress liquidus temperatures by 350–400°C, but liquids at low degrees of melting of a model peridotite remain nepheline–normative. The effect of $CO_2$ is most marked with liquids moving to increasingly undersaturated compositions. Methane saturation produces a similar liquidus depression but results in $OH^-$ solution, low carbon solubility and a reduced melt structure, *i.e.,* Si:O < 1:2.

The studies in the simple Fo–Ne–Qz system are matched by melting studies of several peridotite compositions and by liquidus studies on a variety of magnesian primary magmas from different tectonic settings. Mid-ocean ridge basalts are most commonly deriviative from picritic parents at 15–20 kbar although some low-olivine to quartz tholeiite liquids are probably primary from approximately 8 kbar pressure. However, other primary magmas such as high-magnesium quartz tholeiites and olivine-poor tholeiites and the very siliceous, low-calcium boninite liquids, are derived from much more refractory source rocks than MORB and require two-stage or multistage melting processes. The role of C–H–O fluids in fluxing such multi-stage melting on convergent margins is very important. An additional source of water, accompanied by low $f_{O_2}$ *conditions (i.e.,* $H_2O > CH_4$ fluids) is identified in the redox-interaction of oxidized lithosphere with $CH_4 > H_2$ fluids degassing from the deep earth.

## INTRODUCTION

IN SEEKING to unravel the complexities of magma genesis in the earth's upper mantle, experimental petrologists have successfully demonstrated the diversity of basaltic magmas which can arise from the same source composition by variation of pressure (depth of magma segregation) and temperature (degree of partial melting) (see BASALTIC VOLCANISM STUDY PROJECT, 1981, and references therein). In addressing the same problem, isotope geochemists have demonstrated that mantle-derived magmas have formed from isotopically different sources or reservoirs which have remained isolated and with considerably different ratios of radiogenic elements for long periods of time (BASALTIC VOLCANISM STUDY PROJECT, 1981, and references therein). Some studies of trace element geochemistry have helped to link these two approaches (*e.g.,* FREY *et al.,* 1978), particularly by emphasizing the role played by large differences in partition coefficients between residual crystals and liquids for different elements and have introduced concepts of distinctive behaviour for 'compatible' vs 'incompatible' elements, 'LIL-element', 'HFS' elements, 'light' vs 'heavy' rare earth elements etc.

It is possible that the mantle source regions for primary magmas may be relatively homogeneous in major and compatible elements but quite widely variable in incompatible elements, *i.e.,* those which are perceived as mobile because of high solubility in mantle fluid phase(s) or in small, volatile-rich melt phases. This view finds support from studies of mantle lherzolite samples which provide evidence for multievent histories including late stage enrichment in incompatible elements (BASALTIC VOLCANISM STUDY PROJECT, 1981) and from the recognition of mantle-derived peridotites which are extremely depleted in incompatible elements yet retain major element chemistry with large 'basaltic component' (CaO, $Al_2O_3 > 3$ weight percent; FREY and GREEN, 1974; MENZIES, 1983; KURAT *et al.,* 1980; FREY *et al.,* 1985).

In this paper our major concern is to demonstrate that the mantle source regions for basaltic magmas are inhomogeneous in terms of major elements and that the inhomogeneity arises principally from multistage melting of more primitive mantle lherzolite. Our further purpose is to elaborate the role of C–H–O fluids in controlling the presence or absence of melting and to present arguments for redox-interactions between oxidized ($H_2O + CO_2$)

lithosphere and reduced ($CH_4 + H_2$) deeper mantle, within the tectonic framework of large-scale subduction and transform faulting along convergent margins of lithospheric plates.

We will firstly present data on a simple system forsterite (Fo)–nepheline (Ne)–silica (Qz), as a convenient means of illustrating the principles involved in the study of the multicomponent natural system.

## A SIMPLE SYSTEM ANALOGUE FOR BASALT GENESIS (Fo–Ne–Qz)

YODER and TILLEY (1962) introduced the concept that the broad family of basalts, from olivine nephelinites, through basanites, alkali olivine basalts, picrites, olivine tholeiites to quartz tholeiites and basaltic andesites, could be pictured as a continuum of compositions within the 4-component tetrahedron with apices represented by olivine, quartz, cinopyroxene and feldspathoids. Since that time experimental petrologists have devoted much effort to defining, as functions of pressure and volatile content, the liquidus fields and cotectics, thermal divides and liquid evolution paths within the tetrahedron. Parallel approaches to the problem have used natural basaltic compositions and simple system analogues.

The system forsterite–nepheline–quartz (Fo–Ne–Qz) serves as a simplified analogue of basalt/peridotite in that it contains low melting liquids enriched in sodium aluminosilicate and large liquidus fields for olivine and enstatite. The system has been studied at 28 kbar under dry conditions by WINDOM and BOETTCHER (1981) and GUPTA *et al.* (1986). A pressure of 28 kbar approximates that near the top of the Earth's Low Velocity Zone beneath oceanic lithosphere, *i.e.*, depths of 80–90 km. In terms of mantle magma genesis, the most important boundary in Fo–Ne–Qz is the cotectic between olivine and enstatite which defines the range of liquids formed by increasing degrees of melting of mantle peridotite in the presence of residual olivine and enstatite.

Initial melts (Figure 1) of a model mantle, *i.e.*, olivine + enstatite + jadeite, are 'basanitic' with similar normative nepheline and albite contents. The partial melting involves the reaction Forsterite (Fo) + Jadeite (Jd) → Enstatite (En) + Liquid as the enstatite liquidus surface crosses the Fo–Jd join. With increasing temperature, liquids traverse the base of the simplified basalt tetrahedron passing from nepheline-normative compositions into hypersthene-normative compositions.

We wish to consider melting of two model peridotite compositions, a relatively 'fertile' peridotite (A) (enriched in the low-melting components), and a relatively 'refractory' peridotite (B). It is clear from Figure 1, that although the initial melt composition in each peridotite is the same (at the Fo–En–Jd invariant point) the more refractory peridotite will traverse further along the olivine–enstatite cotectic before enstatite is eliminated as a residual phase. The liquid then moves to 100% melting along the olivine control line passing through the bulk compositions A or B. The positions of the liquidus phase boundaries at 1 bar pressure (SCHAIRER and YODER, 1961) are also illustrated (boundaries to shaded fields of Figures 1 and 2). Liquids formed at 28 kbar along the olivine–enstatite cotectic will crystallize olivine at lower pressure and move towards the 1 bar olivine–enstatite reaction boundary or olivine–albite cotectic as appropriate. The shaded area in Figure 1 illustrates the range of derivative liquids which could be formed by anhydrous melting of both compositions A and B at 28 kbar, followed by crystal fractionation at lower pressure. The area marked by lighter shading includes derivative liquid compositions which could *not* be formed from peridotite A by anhydrous melting followed by crystal fractionation at lower pressure but *could* be formed from the more refractory composition B. In a later section we use this simple system analogue approach to demonstrate that very different

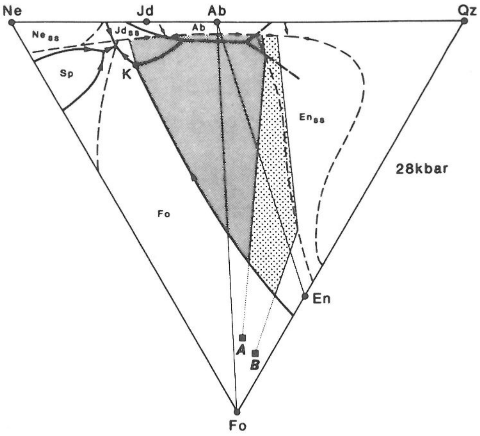

FIG. 1. Liquidus surface of the system Ne–Fo–Qz [weight percent] at 1 bar (dashed lines) and 28 kbar (solid lines) (see text for source references). Liquids formed by melting of a jadeite–enstatite–forsterite assemblage vary from composition K along the olivine–enstatite cotectic until enstatite or olivine is eliminated from the residue. The heavily shaded area includes all liquid compositions which can be derived from model peridotite A by single stage melting at 28 kbar to 1 bar. The more refractory peridotite composition B can yield liquids within the same area but *also* within the lightly shaded area.

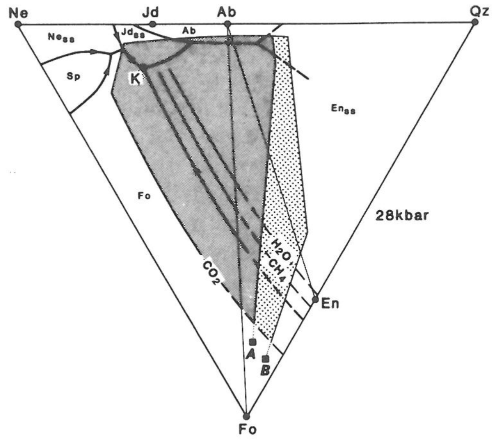

FIG. 2. As for Figure 1 but with the positions of the vapour-saturated cotectic between olivine and enstatite shown for $H_2O$, $CH_4$ and $CO_2$ saturated conditions at 28 kbar. The effect of C–H–O volatiles is to expand the field of possible liquids from peridotites A and B but the restriction of liquids lying in the lightly shaded areas to source compositions such as B, remains valid.

source peridotite compositions are required for MORB and boninite parent magmas.

### *The effect of C–H–O fluids on melting in the Fo–Ne–Qz system*

In Figure 2, the position of the forsterite-enstatite cotectic at 28 kbar in the vapour-absent Fo–Ne–Qz system is compared with the positions of the same cotectic under vapour-saturated conditions, the three specific cases illustrated being $H_2O$-saturated, $CO_2$-saturated and $CH_4$-saturated (EGGLER, 1978; TAYLOR, 1985; GREEN *et al.*, 1986). The effect of water is to expand the olivine field at the expense of enstatite (KUSHIRO, 1972) but liquids at low degrees of partial melting remain strongly silica-undersaturated and nepheline-normative (EGGLER, 1975). Water enters the melt as $OH^-$, causing depolymerization by hydrolysis of Al–O–Si and Si–O–Si bonds and depression of the liquidus by 350–400°C. In contrast, $CO_2$ enters the melt at $CO_3^{2-}$ in the form of metallocarbonate complexes resulting in melt polymerization and marked expansion of the liquidus field of enstatite at the expense of forsterite (see earlier discussions by EGGLER, 1978; BREY and GREEN, 1975, 1976; MYSEN and BOETTCHER, 1975; MYSEN *et al.*, 1980, and others on related systems). Liquids at low degrees of melting are nepheline-rich (Ne > Ab) and approach simple system analogues of olivine nephelinite.

Under $CH_4$-saturated conditions, liquidus temperatures are depressed by 80–90°C at 28 kbar (see also EGGLER and BAKER, 1982). Electron microprobe, gas chromatographic analyses and infrared spectroscopic studies show carbon solubilities up to 0.2% carbon (*i.e.*, ~0.25% $CH_4$ or ~0.7% $CO_2$ equivalent) and OH solution equivalent to 2–3 weight percent $H_2O$. The effect of methane-saturation is to expand the field of olivine at the expense of enstatite (Figure 2) but to a lesser extent than $H_2O$-saturation (see also EGGLER and BAKER, 1982). The infrared spectroscopic study of quenched glasses shows changes in the absorption bands attributed to the aluminosilicate network which suggest an increase in the Si:O ratio (*i.e.*, >1:2) of the network (TAYLOR, 1985; TAYLOR and GREEN, 1987). Thus, under methane-saturated conditions, melts may become *reduced* and contain small dissolved carbon and larger $OH^-$ contents. On decompression, without redox-interaction with wall-rocks, such melts will exsolve $CH_4 + H_2$. It is noteworthy that initial melts near the low temperature minimum melting for jadeite-enstatite-forsterite, remain nepheline normative in all three cases illustrated in Figure 2. However, the degree of undersaturation is sensitively dependent on the fluid phase present.

In considering melting in the upper mantle, the evidence from mantle-derived liquids and xenoliths, from the presence of graphite and diamond and fluid inclusions within mantle samples, argue that mantle fluids are dominated by the C–H–O system. In considering melting in the upper mantle, it is necessary to consider possible variations on fluid phase compositions within the C–H–O system and whether particular source regions may be characterized by particular fluid phase characteristics. The simple system analogue illustrated in Figure 2 shows that variation in fluid phase composition will not invalidate one of the major conclusions from Figure 1, that is, that some specific liquids and potential source peridotite compositions cannot be related to each other because of limitations imposed by their major element compositions and phase relations.

## FLUID-CONTROLLED MELTING IN THE UPPER MANTLE

The importance of water in determining the pressure–temperature conditions and form of the mantle solidus is well determined from studies on peridotite compositions (KUSHIRO, 1968; GREEN, 1973; MYSEN and BOETTCHER, 1975). The model 'pyrolite' composition studied (GREEN, 1973) may

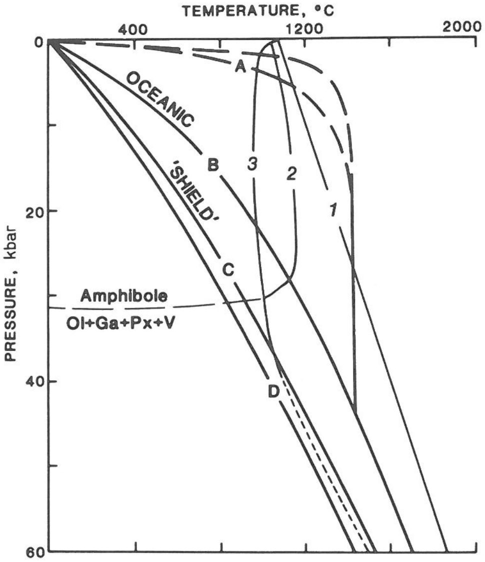

FIG. 3. Solidi for mantle peridotite ('Hawaiian' pyrolite) (GREEN, 1973): (1) Anhydrous (2) $0 < H_2O < 0.4$ weight percent (Amphibole dehydration solidus) (3) $H_2O > 0.5$ weight percent = water-saturated solidus. Also shown are geothermal gradients for mature oceanic crust (B), 'shield' regions (C, D) and near-mid ocean spreading centres (A) (BASALTIC VOLCANISM PROJECT, 1981; Figure 9.5.7). Ol, olivine; Px, pyroxene; Ga, garnet; V, vapour.

be referred to as 'Hawaiian pyrolite' composition as the 'melt' component in the 'melt + residue' model used to calculate the model 'pyrolite' composition (RINGWOOD, 1966), was based on Hawaiian olivine tholeiite liquids, *i.e.*, enriched in $TiO_2$, $K_2O$ and incompatible elements relative to MORB. In Figure 3, the solidi for three distinctive water contents are illustrated:

(1) Anhydrous solidus

(2) Dehydration solidus; pargasitic hornblende is present on the solidus below 28–29 kbar but the water content is less than approximately 0.4 weight percent.

(3) Water-saturated solidus; pargasitic hornblende is present on the solidus but water content exceeds approximately 0.4 weight percent so that water is present in excess and sub-solidus assemblages coexist with a water-rich fluid.

In Figure 3 we illustrate geothermal gradients appropriate to thermal upwelling beneath spreading centres (A), beneath 'old' oceanic crust and lithosphere (B) and beneath ancient Archean crust and lithosphere (C, D) (BASALTIC VOLCANISM PROJECT, 1981; Figure 9.5.7, p. 1180). The presence or absence of a region of partial melting along geotherms B, C and D and the depth to such a region is clearly sensitively controlled by the role of water, specifically by the activity of water.

Recognising that carbon, as well as water, is a component of mantle fluids adds further complexity to the determination of the mantle solidus. It is necessary to determine the activity of water in the C–H–O system under mantle conditions. TAYLOR (1985, 1986) has presented a thermodynamic model of this system appropriate to mantle pressures and temperatures. Results may be presented, following FROST (1979) as isobaric, isothermal diagrams plotting $\log f_{O_2}$ vs $X_C$* defined as the mole fraction of carbon relative to hydrogen in the bulk fluid.

In Figure 4 and Table 1 we illustrate results at 30 kbar, 1327°C showing the carbon–saturation surface bounding the metastable carbon-oversaturated fluid field (TAYLOR 1985, 1986). The strong dependence of fluid composition on oxygen fugacity is very clear in Figure 4 and Table 1 and it is noteworthy that graphite coexists with fluid approaching pure water in composition at $f_{O_2}$ = IW + 1 to 2 log units.

The composition of C–H–O fluids present along geothermal gradients in Archean shield and in oceanic crust regions (taken from Figure 9.5.7, p. 1180, BASALTIC VOLCANISM STUDY PROJECT, 1981) can be calculated from this thermodynamic

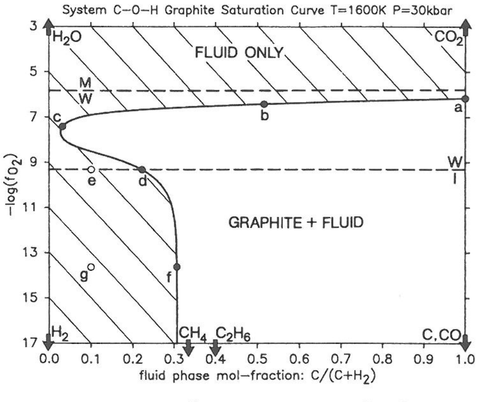

FIG. 4. Log $f_{O_2}$ vs $X_C$ $\left[=\text{mol fraction } \frac{C}{(C+H_2)}\right]$ diagram at 1600 K (1327°C), 30 kbar showing the graphite saturation surface, stable fluid–only pseudo-divariant region (blank) and $X_C$–independent traces of IW and MW oxygen buffers. Arrows indicate the off-scale positions of the six C–O–H volatile species, filled circles ('a' to 'f') on the graphite saturation surface correspond to fluid compositions given in Table 1. The maximum mol fraction of $H_2O$ on the graphite saturation curve is reached at point C.

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* $X_C = x_{CO} + x_{CO_2} + \frac{1}{3}x_{CH_4} + \frac{2}{5}x_{C_2H_6}$.

Table 1. Fluid compositions at selected points in Figure 6; $T$ = 1600 K, $P$ = 30 kbar

EQUILIBRIUM FLUIDS
Mol percent species*

| | $-\log f_{O_2}$ | $X_C$ | $X_O$ | $H_2O$ | $CO_2$ | $CO$ | $H_2$ | $CH_4$ | $C_2H_6$ | $V^{mix}cm^3/mol$ |
|---|---|---|---|---|---|---|---|---|---|---|
| a** | 6.15 | 1.000 | 1.000 | 0 | 97.1 | 2.9 | 0 | 0 | 0 | 30.27 |
| b | 6.40 | 0.510 | 0.671 | 48.5 | 49.3 | 1.6 | 0.4 | 0.1 | 0 | 24.21 |
| c† | 7.40 | 0.032 | 0.339 | 94.1 | 2.3 | 0.2 | 1.5 | 1.9 | 0 | 17.90 |
| d‡ | 9.30 | 0.220 | 0.091 | 26.9 | 0.1 | 0.1 | 7.8 | 63.3 | 1.8 | 25.60 |
| e‡ | 9.30 | 0.100 | 0.192 | 57.4 | 0 | 0 | 12.7 | 29.7 | 0.2 | 21.05 |
| f | 13.60 | 0.306 | 0.001 | 0.2 | 0 | 0 | 8.7 | 87.7 | 3.4 | 28.69 |
| g | 13.60 | 0.100 | 0.004 | 0.2 | 0 | 0 | 68.8 | 29.9 | 0 | 19.83 |

** $f_{O_2}$ = GCO, † $f_{O_2}$ = GW(max.$x_{H_2O}$), ‡ $f_{O_2}$ = IW.
* round-off error = ±0.1 mol percent.

model provided that we assume that graphite or diamond is a stable accessory mantle mineral. The C–H–O fluid composition at any pressure and temperature is only fixed if $f_{O_2}$ is also known—in Figure 5 (GREEN *et al.*, 1986) we calculate fluid compositions for the two geothermal gradients assuming $f_{O_2}$ = FMQ, IW + 2 log units and IW, respectively. The results in Figures 4 and 5 demonstrate that if mantle $f_{O_2}$ conditions are near IW to IW + 2 or 3 log units, then mantle fluids are dominated by water or water + methane. In the presence of a mixed fluid, ($H_2O + CH_4$), pargasitic hornblende will reach a maximum thermal stability near $a_{H_2O} \sim 0.5$ (see study by HOLLOWAY (1973) on pargasite + $CO_2$ + $H_2O$)—an interpretation supported by studies in progress in which subsolidus amphibole + garnet lherzolite crystallized at 25 kbar, 1100°C in the presence of graphite and an $f_{O_2}$-buffered fluid phase of $CH_4$:$H_2O$ ~ 1:1.

There is evidence from measurements of intrinsic oxygen fugacity of mantle minerals, of deep-seated igneous intrusions and from identification of reduced gases ($CH_4$) evolving from MORB glasses and from submarine volcanic centres (ARCULUS *et al.* 1984; SATO and VALENZA, 1980; WELHAN and CRAIG, 1979, 1983) that the earth's mantle in the source regions for basaltic magmas is reduced with $f_{O_2}$ ~ IW to IW + 1 to 2 log units. These interpretations are not unchallenged and others, for example, EGGLER (1983) and MATTIOLI and WOOD (1986) infer higher mantle $f_{O_2}$ conditions. At near-surface and shallow crustal conditions, mineral assemblages of igneous rocks indicate $f_{O_2} \geq$ FMQ (HAGGERTY, 1978; SATO, 1978). Thus, the earth's lithosphere may be seen broadly as a transition zone or boundary layer between deeper mantle with $f_{O_2}$ ~ IW and mantle fluids dominated by $CH_4$, $H_2O$ + $H_2$ and near-surface conditions with $f_{O_2}$ ~ FMQ and fluids dominated by $H_2O$, $CO_2$. The consequences of this redox interaction, coupled with the sensitivity of the mantle solidus to $a_{H_2O}$, are explored more fully elsewhere (GREEN *et al.*, 1986) but are presented in summary form in the following section and Figures 6 and 7 which also build upon ideas canvassed by others including WYLLIE (1978, 1979, 1980), WOERMANN and ROSENHAUER (1985), EGGLER (1978), EGGLER and BAKER (1982), RYABCHIKOV *et al.* (1981) and GREEN (1973).

### *Mantle degassing and magma genesis: Oceanic lithosphere*

We adopt the view that the earth's upper mantle *beneath the asthenosphere* is at $f_{O_2}$ ~ IW ± 1 log unit and that this region contains C–H–O fluids, possibly remnant from primordial entrapped volatiles, and minor carbon (diamond) contents. (In adopting this view we recognize that alternative views of higher oxygen fugacity (QFM to MW) are also current and our purpose is to explore the 'reduced mantle' model.) The fluids will be dominated by $CH_4 > H_2O > H_2$, $C_2H_6$ (*cf.* GOLD and SOTER, 1980, 1983). The transition from these reduced conditions towards more oxidized lithosphere will result in fluid change with increase in $H_2O$:$CH_4$ (Figures 4 and 5) but the oceanic geothermal gradient will lie within a field of partial melting at $P$ > 28–29 kbar (Figure 3) due to instability of pargasitic hornblende and the role of water in depressing the mantle solidus. Provided that fluid concentrations are low, this region of partial melting will be a fluid-absent region in which a minor melt phase can accommodate continuously variable $f_{O_2}$ via melt structure redox changes (SiO variation) with solubility of $OH^-$ and minor carbon, and at higher $f_{O_2}$, by increasing solubility of $CO_3^{2-}$. At depths < 90 km, the stability of pargasitic hornblende at $f_{O_2}$ ~ IW + 1 to 3 log units creates a lid

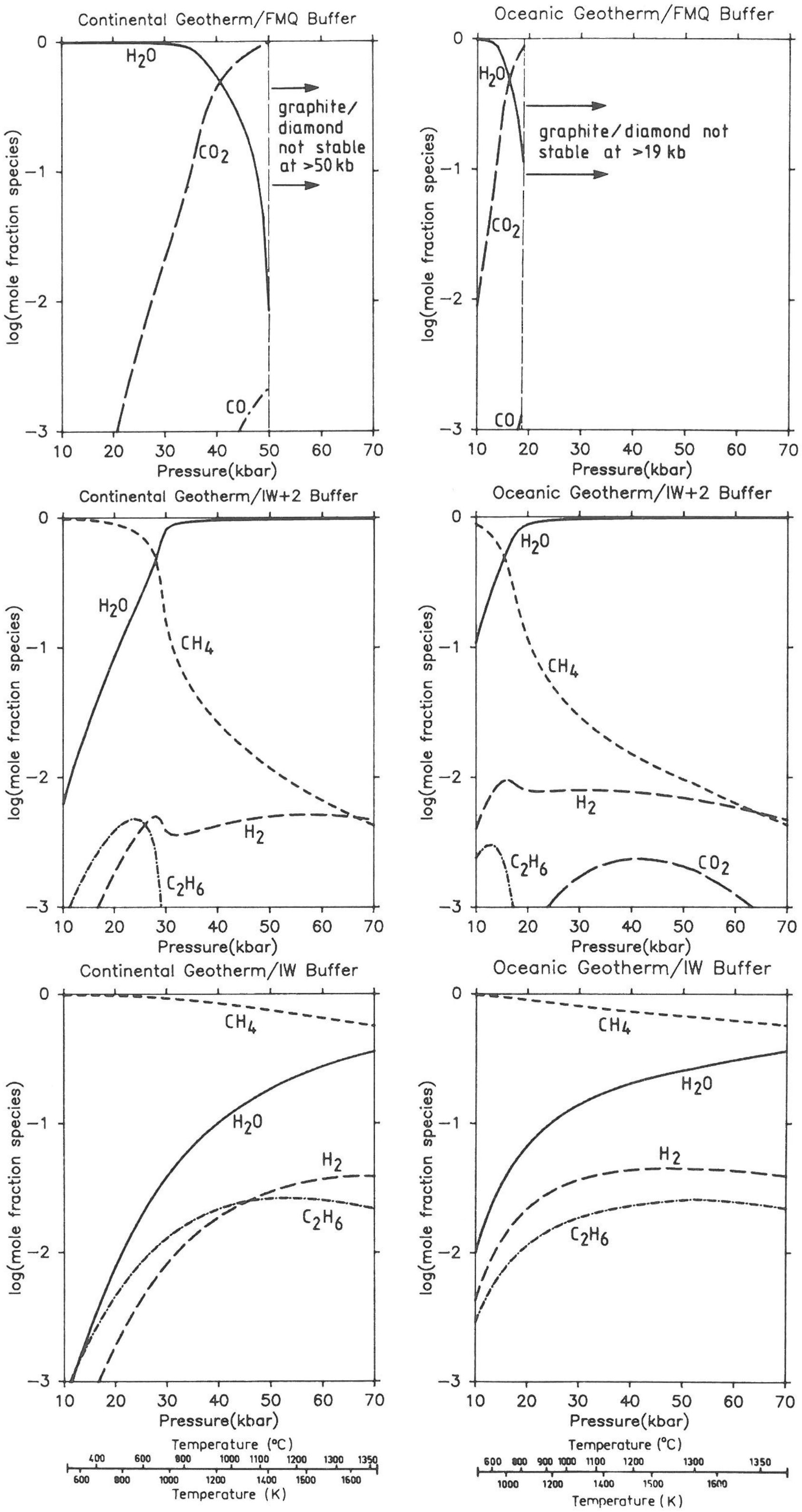

FIG. 5. Fluid compositions along model ‘oceanic’ and ‘shield’ geotherms (BASALTIC VOLCANISM STUDY PROJECT, 1981; Figure 9.5.7, p. 1180) assuming fluid coexists with graphite/diamond and with specific $f_{O_2}$’s corresponding to IW, IW + 2 log units and FMQ buffers.

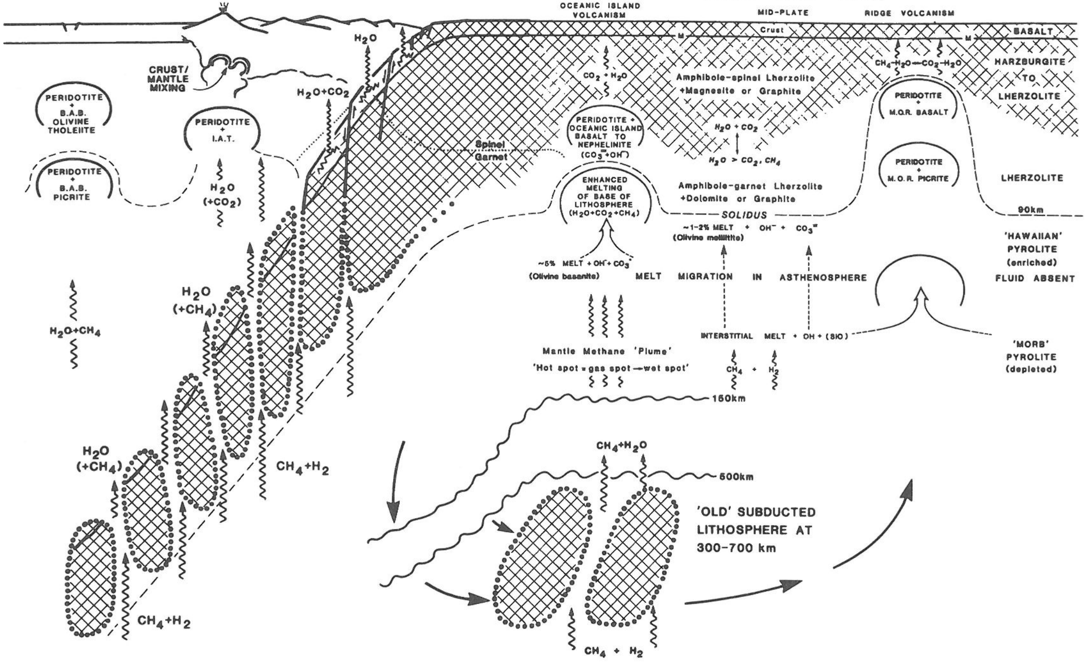

FIG. 6. Schematic model of the oceanic lithosphere and asthenosphere. The lithosphere is variable in composition due to melt extraction and fluid enrichment events and is envisaged as variably oxidized from FMQ (shaded areas) to ~IW + 1 to 2 log units (blank areas of lithosphere). The asthenosphere is a fluid–absent region in which C–H–O volatiles are dissolved in a small melt fraction (1–2% melt) which migrates towards the top of the asthenosphere or base of the lithosphere. Source regions for Hawaiian–type island chains (hot–spots) are in the upper part of the asthenosphere or base of the lithosphere. Source regions for MORB are in the lower part of the asthenosphere. The mantle is degassing reduced fluids ($CH_4 + H_2$) and the asthenosphere is a fluid–absent region with intrinsic oxygen content and fugacity varying from ~IW to IW + 2 to 3 log units—this variation is accommodated in change of melt structure from reduced (Si:O > 1:2) to contain $OH^-$ and $CO_3^{2-}$ ($f_{O_2}$ ~ IW + 2 to 3 log units). The patterned symbol on the oceanic lithosphere signifies $f_{O_2}$ ~ FMQ, *i.e.*, 'oxidized' lithosphere. In the convergent margin or subduction plate boundary scenario, the oxidized lithosphere is portrayed as penetrated along fracture zones by $CH_4 + H_2$ fluids from subjacent mantle. The redox–interactions produce $H_2O$–rich fluids which strongly influence melting relations above or within the subducted lithosphere. Thus, even at depths below those at which hydrated minerals of the oceanic crust and lithosphere have been lost, the 'slab' may be a source of $H_2O$–rich fluids. Abbreviations for primary magmas developed within the schematic diapirs are: M.O.R. = mid–ocean ridge; I.A.T. = island arc tholeiite; B.A.B. = back–arc basin. See text for further discussion, including the genesis of boninite parent magmas.

to the partially molten layer because any interstitial melt migrating upwards from the asthenosphere will crystallize to pargasite–bearing lherzolite containing graphite or dolomite ± graphite (GREEN, 1973; EGGLER, 1978; WYLLIE, 1978; GREEN *et al.*, 1986).

In Figure 6, the asthenosphere beneath oceanic crust is a fluid–absent region separating methane–rich fluids in the deep mantle from $H_2O$–rich and $H_2O + CO_2$ fluids in the lithosphere. It is a zone of decoupling between lithospheric plates and underlying mantle, a zone of increased seismic attenuation and decreased seismic velocity (GREEN and LIEBERMANN, 1976; GREEN, 1973; EGGLER, 1978; WYLLIE, 1978) and most importantly, a zone of chemical differentiation rather than homogenization due to the migration of an interstitial melt phase towards the top of the asthenosphere. The character of the interstitial melt is extremely undersaturated olivine melilitite to olivine nephelinite (GREEN, 1971; GREEN and LIEBERMANN, 1976; BREY and GREEN, 1976; WYLLIE, 1979; EGGLER, 1978; WENDLANDT and MYSEN, 1980) and apart from enriching the upper part and depleting the lower part of the asthenosphere in incompatible elements, the high Ca/Al ratio of olivine melilitite will decrease the Ca/Al ratio of the lower part of the astheno-

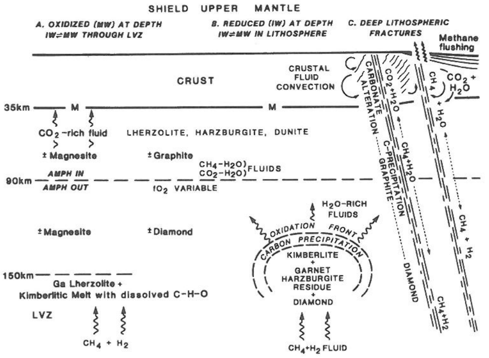

FIG. 7. Schematic model for the continental lithosphere beneath Archean/Proterozoic shield regions. See text for detailed discussion. The deep mantle is degassing ($CH_4 + H_2$) fluids that interact with oxidized lithosphere. (A) suggests a deep, thin asthenospheric layer (partial melting) in which the $f_{O_2}$ change from mantle or lithosphere is accommodated within the fluid–absent melt. (B) suggests a mechanism of 'redox' melting (see text) in which diamond-bearing garnet harzburgite is left as a residue from oxidation of $CH_4 + H_2$ to $H_2O$ + C with extraction of water–rich kimberlitic melt. (C) suggests a role for deep lithosphere fractures in localizing mantle fluid release and interaction of these fluids with oxidized crustal fluids at shallow depths.

sphere and increase the Ca/Al ratio of the uppermost part. The extent of chemical differentiation will be related to: (a) the age of the lithosphere, (b) the extent to which volumes of old lithosphere/asthenosphere are preserved near transform fault/spreading centre intersections or at spreading axes themselves, and (c) depth within the asthenosphere. The base of the lithosphere will also become enriched in incompatible elements, hosted particularly in pargasitic hornblende, phlogopite and apatite as minor and accessory phases. In Figure 6, the lower part of the asthenosphere is depicted as a fluid–absent region at low $f_{O_2}$ (IW to IW + 1 log unit) which has the incompatible element contents appropriate to MORB source (abbreviated as 'MORB' pyrolite) whereas the upper part of the asthenosphere has $f_{O_2}$ near IW + 2 to 3 log units and incompatible element contents appropriate to source regions for tholeiites of oceanic island chains such as Hawaii ('hot spot' source regions, abbreviated as 'Hawaiian pyrolite').

The relationships between magmatism at spreading centres, at 'hot spots' or migrating tension fractures (see Figure 6) and the chemically zoned asthenosphere has been fully explored elsewhere (GREEN, 1971, 1972; GREEN and LIEBERMANN, 1976; GREEN *et al.,* 1986) and in this paper we address the possibilities created by interaction of an oxidized subducted lithospheric slab with reduced mantle below the asthenosphere (Figure 6).

It is generally accepted that the peridotite of the lithosphere is variable in composition from lherzolite to harzburgite, probably as a result of prior extraction of basaltic to picritic melts. Local, more extreme chemical variation results from trapped liquids, high-pressure accumulates or metasomatic enrichment from migratory fluid phases. Two examples of chemical variation are illustrated in Figure 8, showing chemical trends in spinel lherzolite inclusions from W. Victoria (NICKEL and GREEN, 1984) and from garnet and spinel lherzolites within the Ronda high–temperature, high–pressure peridotite intrusion (FREY *et al.,* 1985). Even more refractory harzburgite compositions are seen in some ophiolite complexes. These are commonly partially or completely serpentinized and during serpentinization, became highly oxidized with abundant magnetite development.

The evidence from deep focus earthquakes suggests that subducted lithospheric slabs retain their identity to depths of at least 600–700 km. Dehydration reactions in subducted basaltic crust and serpentinized peridotite may lead to migration of $H_2O$-rich or $H_2O + CO_2$ fluids from the subducted slab into the overlying peridotite wedge, instigating melting on the water–saturated peridotite solidus (solidus 3 of Figure 3, KUSHIRO 1968; GREEN, 1973). Melts formed in this way will have geochemical characteristics reflecting the partially residual character of the remobilized lithosphere together with the imprint of components partitioned into

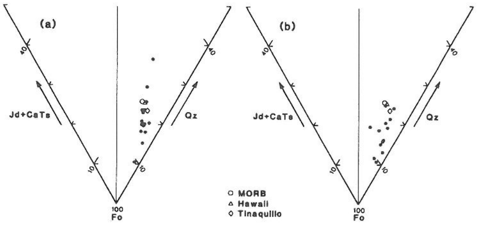

FIG. 8. Two examples of peridotite suites of variable composition from lherzolite to harzburgite, reflecting prior extraction of basaltic to picritic melts, plotted in the normative system Fo–Jd + CaTs–Qz–Di, projected from Di onto the plane Fo–Jd + CaTs–Qz. (a) Ronda, high temperature, high pressure peridotite intrusion FREY *et al.,* 1985; (b) Spinel lherzolite inclusions from Lake Bullenmerri, W. Victoria, NICKEL and GREEN, 1984. Also plotted are 'MORB' pyrolite, 'Hawaiian' pyrolite and Tinaquillo lherzolite compositions, which have been studied experimentally under high pressures and temperatures (JAQUES and GREEN, 1980; FALLOON and GREEN, unpublished data).

and transported by the fluid phase migrating from the subducted slab. A related model suggests that temperatures on the upper part of the subducted slab (the subducted basaltic/eclogitic crust particularly) may be high enough for fluid–saturated or dehydration melting and for melt to migrate from the subducted slab to modify and melt the overlying peridotite mantle wedge. The models have been explored and evaluated in many previous publications (see RINGWOOD (1974) and GILL (1981) for review and references). However the concept of redox–interaction between deep mantle degassing $CH_4 + H_2$–rich fluids and lithospheric slab with mineral assemblages reflecting $f_{O_2}$ near FMQ to MW conditions adds a further dimension to subduction. It is possible for dehydrated, very refractory peridotite or eclogite of the subducted slab to generate $H_2O$–rich fluid by reaction of anhydrous oxidized mineral assemblages ($Fe^{3+}$ in silicates, spinels, carbonates) with primary $CH_4 + H_2$ fluids. The increased $a_{H_2O}$ will cause melting, even of refractory harzburgite (KUSHIRO, 1972; MYSEN and BOETTCHER, 1975; GREEN, 1973). A second, important effect will be that any redox front bounding a residual slab of subducted lithosphere in contact with normal MORB pyrolite will be a locus for high $a_{H_2O}$—the mechanical effect of this will be to concentrate stress release (earthquake activity) at such redox fronts. Lower temperatures within the subducted slab will generally inhibit melting of the slab itself but this may be counteracted by high $a_{H_2O}$ contrasting with high $a_{CH_4}$ and thus high solidus temperatures in surrounding mantle. A particularly favourable location for redox interaction coupled with higher temperatures at the edges of a subducted slab will be at trench/transform intersections, *e.g.*, the south end of the Marianas Trench and the northern end of the Tonga Trench, where the subducted slab abuts, across a transform fault zone, against normal oceanic lithosphere/asthenosphere to deep levels. The movement zone will probably act as a channel–way for enhanced mantle degassing and by providing a temperature contrast across the transform fault zone, will act as a heat input to the subducted slab.

In Figure 6, we suggest that the immediate source peridotite for Hawaiian or 'hot spot' volcanism lies in the uppermost part of the asthenosphere or alternatively within the base of the lithosphere, where this has been enriched by migration, reaction and crystallization of an interstitial melt. The success of the 'fixed hot spot' frame of reference in analyzing relative plate movement over the past 100 million years shows that the cause or trigger for island chain or 'hot spot trace' volcanism does not lie within the moving lithospheric plate but lies beneath this plate and reflects a 'fixed' mantle or a deep mantle in which the convective flow is much slower than and decoupled from the lithospheric plate motions (MORGAN, 1972; DUNCAN, 1981). If large slabs of subducted lithosphere are carried to depths > 600 km and embedded within the return flow or deeper mantle convection pattern (HOFFMAN and WHITE, 1982; RINGWOOD, 1986), then they may act to oxidize $CH_4 + H_2$ fluids passing through them to $CH_4 + H_2O$. This effect could feed $CH_4 + H_2O$ plumes into overlying asthenosphere + lithosphere and trigger 'hot spot volcanism' as depicted in Figure 6. For example we suggest that the great frequency of sea mounts and island chain volcanoes in the West Pacific may be due to the Pacific plate over-riding relict subducted slabs embedded in the 150–650 km depth interval of the upper mantle and reflecting material originally subducted on Palaeozoic-Mesozoic subduction zones along the East Asian margin.

### *Mantle degassing and magma genesis: Continental lithosphere*

In Figure 7 (*cf.* GREEN *et al.*, 1986) we present a summary diagram illustrating mantle degassing of $CH_4 + H_2$ beneath a very old, thick lithosphere characterized by very low geothermal gradient (Shield geotherms C and D of Figure 3). The lithosphere has a zone of amphibole stability in lherzolitic compositions at $P < 28$–$29$ kbar but at deeper levels subsolidus assemblages contain phlogopite and may contain other hydrous phases such as titanoclinohumite (MCGETCHIN *et al.*, 1970). Carbon will be present as diamond or graphite, or at depths > 150 km, as magnesite if $f_{O_2} >$ FMQ (Figure 5; EGGLER 1975, 1978; GREEN *et al.*, 1986; BREY *et al.*, 1983; WYLLIE, 1978, 1979). Samples of deep continental lithosphere occur as xenoliths in kimberlite pipes and illustrate heterogeneity and variations from possible trapped liquids or relict subducted oceanic crust (eclogite, grosspydite, lherzolite to highly refractory harzburgite, and extremely K– and Ti–rich phlogopite rocks).

If mantle temperatures approach the solidus 3 (Figure 3), then redox melting of lithosphere may occur by interaction of reduced $CH_4$–rich fluids from deeper levels with oxidized lherzolite, or harzburgite. GREEN *et al.* (1986) have suggested that the distinctive mineral inclusion suite within South African diamonds which is characterized by extremely magnesian olivine, refractory low–Al enstatite and extremely low calcium, Cr–rich pyrope garnet, is a consequence of redox melting (see Figure 7, scenario B).

Although Archaean and Proterozoic cratons preserve a remarkably long history of stability as recorded by cover of undeformed Proterozoic sediments, they are frequently cut by mafic dyke swarms. In the post–Permian breakup of Gondwanaland, stable cratons with thick underlying lithosphere, have rifted and drifted apart so that regions of old, thick lithosphere are now juxtaposed against young lithosphere of oceanic type. An initial situation of rapid temperature change at the base of the lithosphere of a newly rifted craton (*cf.* Boyd 1973; Boyd and Nixon, 1975; Nickel and Green, 1985) will be followed by heating of the sub–craton lithosphere so that the solidus of phlogopite–bearing lherzolite and harzburgite will be exceeded. Small melt fractions of olivine lamproite to leucite lamproite composition (Foley, 1986; Foley *et al.*, 1986) reflect phlogopite harzburgite source rocks and depths of segregation from 150 km to ~70 km respectively. Source rocks of phlogopite–bearing garnet lherzolite will produce potassic olivine nephelinites to basanites (Wedepohl, 1985) with the particular liquid composition being determined by $CO_2$:$H_2O$ as well as by source rocks and depth of magma segregation (Frey *et al.*, 1978; Eggler, 1978; Green, 1976; Brey and Green, 1976; Wyllie, 1979). If upwelling and diapirism occurs from within the heated former sub–cratonic lithosphere, then magmas produced at lower pressures will retain trace element and isotopic compositions reflecting their source compositions but the magmas will be picritic to tholeiitic or alkali olivine basaltic in character, reflecting higher degrees of melting and shallower depths of magma segregation.

## MAGMA SOURCE COMPOSITIONS

### *Mantle–derived peridotite suites*

Compositions of two suites ranging from lherzolite to harzburgite and with high pressure mineral assemblages requiring crystallization at pressures in excess of 10 kbar are projected in Figure 8. The Ronda peridotite suite (Frey *et al.*, 1985) defines a linear trend consistent with extraction of magma lying within the olivine–hypersthene–plagioclase–diopside volume, *i.e.*, an olivine tholeiite or tholeiitic picrite liquid (Frey *et al.*, 1985). The Bullenmerii suite shows more scatter but again a trend implying an olivine tholeiite or tholeiitic picrite extraction (*cf.* Nickel and Green, 1984). Model Hawaiian pyrolite, MORB pyrolite and Tinaquillo lherzolite compositions are also plotted in Figure 8. All three have CaO and $Al_2O_3$ contents > 3–4 weight percent but the suites differ in $Na_2O$, $TiO_2$, $K_2O$, and incompatible element contents with Tinaquillo being the most refractory composition (Jaques and Green, 1980; Green *et al.*, 1979).

The trends in Figure 8 defined by the mantle samples (which could be matched by other xenolith suites or high–temperature, high–pressure intrusive peridotite suites) are considered to result from partial melting and incomplete melt extraction (Frey *et al.*, 1985; Nickel and Green, 1984) and thus we infer that mantle source compositions, prior to melt extraction are at least as 'fertile' as the most plagioclase–rich and diopside–rich limits of the trends shown in Figure 8. If the processes outlined in previous sections, which lead to one or more remelting events, particularly under the fluxing effects of C–H–O fluids, are operative in the earth, then the range of potential source peridotite compositions covers at least the range of the samples plotted, *i.e.*, trending from lherzolite towards harzburgite with 80 weight percent Ol, 20 weight percent En.

### *Source for mid-ocean ridge basalts*

Compositions of (>70) glasses from dredged ocean floor basalts are plotted in Figures 9 and 10—all have 100 Mg/(Mg + $Fe^{2+}$) > 68, *i.e.*, they are primitive in the sense of suitability as melts in equilibrium with olivine > $Mg_{87}$. It may be noted that

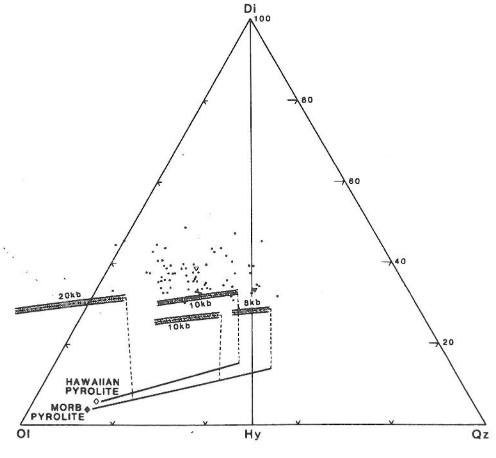

FIG. 9. Equilibrium partial melts of MORB pyrolite at 8, 10 and 20 kbar (Falloon and Green, unpublished data) and 'Hawaiian' pyrolite at 10 kbar (Jaques and Green, 1980) compared with primitive MORB glasses in the normative system Ol–Jd + CaTs–Qz–Di. Compositions are projected from plagioclase (An + Ab) onto the plane Ol–Di–Qz. Cotectics are as follows: (1) stippled line, ol + opx + cpx + L cotectic. (2) dashed line, ol + opx + L cotectic. (3) solid line, ol + L cotectic. (▼) is the MORB glass DSDP3–18–7–1, studied by Green *et al.*, (1979) and (▽) is the low-olivine parent composition of Bryan (1979).

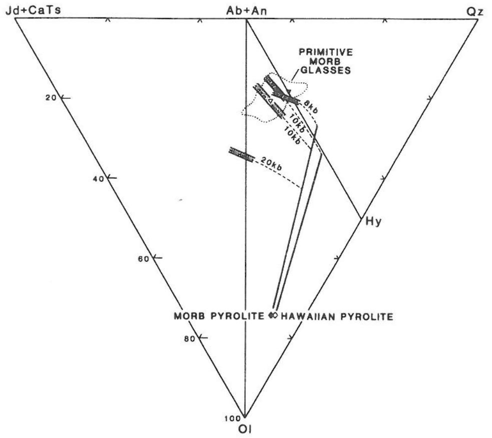

FIG. 10. Equilibrium partial melts of 'MORB' pyrolite at 8, 10 and 20 kbar and 'Hawaiian' pyrolite at 10 kbar compared with the field of primitive MORB glasses in the normative system Ol–Jd + CaTs–Qz–Di. Compositions are projected from Di onto the plane Jd + CaTs–Qz–Ol. Cotectics and symbols as for Figure 9. For purposes of clarity the primitive MORB glasses are not plotted individually as in Figure 9 but outlined by the dotted line.

olivine tholeiite liquids dominate the group but they do spread from quartz–normative compositions (5 points) to nepheline–normative compositions (2 points). The glass DSDP 3–18–7–1, studied experimentally by GREEN *et al.*, (1979) as a primitive MORB lies centrally within the MORB field.

GREEN *et al.* (1979, Table 4, column D) calculated a model source composition for DSDP 3–18–7–1 and we have studied the anhydrous melting relationships of this composition (MORB pyrolite) from 8–20 kbar. A 'sandwich' technique (STOLPER, 1980) was used in which a layer of DSDP 3–18–7–1 glass is placed between two layers of MORB pyrolite. The bulk compositions of these mixtures lie in the join between these two compositions (Figures 9 and 10). This approach avoids the bulk compositional changes inherent in equilibrating diverse liquids within unrelated peridotite layers (FUJII and SCARFE, 1985; TAKAHASHI and KUSHIRO, 1983; STOLPER, 1980) although these studies provide useful comparative data for our purposes.

The results are summarized in Figures 9 and 10, showing 3–phase cotectics (Ol + Opx + Cpx), followed by (Ol + Opx) cotectics until the olivine-control line is reached as the temperature increases. Attention is particularly drawn to the compositional range of liquids along the 3–phase cotectic. For example, at 20 kbar liquids in equilibrium with olivine, orthopyroxene and clinopyroxene range from nepheline–normative picrites to picrites with low normative hypersthene contents, before clinopyroxene disappears. Examination of Figure 10 alone would suggest that MORB glasses may be explained as primary olivine tholeiite melts separating from Ol + Opx + Cpx residues at approximately 8 kbar to 13 kbar pressure. Limited olivine fractionation and variation in percent melting could possibly account for the observed compositional variation of Figure 10. However, it is insufficient to examine only one projection or plot of the many chemical variables involved. From Figure 9, it is clear that almost all MORB glasses are too rich in normative diopside to have formed as primary liquids on Ol + Opx + Cpx cotectics. However, a few exceptions lie close to Ol + Opx + Cpx cotectics at ~8 kbar and these distinctive MORB glasses have low normative olivine contents or are quartz normative. They are similar in composition to the low–olivine parent composition of BRYAN (1979) and are consistent with being close to primary liquids or derived from ~8 kbar primary olivine tholeiite magmas via limited olivine fractionation.

Examination of Figure 9 suggests that liquids formed by small degrees of melting at 10–12 kbar, might fractionate small amounts of olivine to reach MORB glass compositions. In fact, this mechanism does not work as liquids at small degrees of melting have $TiO_2$ contents, Na/Ca ratio, $K_2O$ contents and $P_2O_5$ contents that are too high for MORBs.

The data, as illustrated in Figures 9 and 10, but confirmed by other oxide, element ratio and normative plots, show that most MORB glasses are derivative by olivine factionation from primary picritic magmas (*i.e.*, liquids with >20% normative olivine), segregating from residual olivine, orthopyroxene and clinopyroxene at pressures of 15–20 kbar. Melting conditions are essentially anhydrous although small quantities of reduced and oxidised volatiles may be present (BYERS *et al.*, 1983; MATHEZ, 1984). It is inferred from Figure 10 particularly, that we do not see liquids formed by very high degrees of melting along the olivine + orthopyroxene cotectic and we believe that this is unlikely in a single stage melting process as such liquids would require >30–35% melting and melt segregation apparently occurs prior to this (GREEN and RINGWOOD, 1967; MYSEN and KUSHIRO, 1977; JAQUES and GREEN 1980).

Liquids at 10 kbar from the Hawaiian pyrolite melting study (JAQUES and GREEN, 1980) are also plotted in Figure 10. The pattern of liquid variation with progressively higher degrees of melting is similar to that for MORB pyrolite but the Ol + Opx + Cpx cotectic is at much higher normative diopside contents. Although the cotectic overlaps the MORB field in this projection the liquids have >3 weight percent $TiO_2$, >0.5 weight percent $K_2O$ and Na/Ca ratios unlike MORB. The Hawaiian pyrolite composition cannot produce MORB liquids in terms of major and minor elements and vice versa—different source compositions are required.

### *Source for Troodos Upper Pillow Lavas*

CAMERON (1985) has subdivided the Troodos Upper Pillow Lavas into three chemical groups with trace element and isotopic abundances requiring chemical differences between the source compositions for each group. DUNCAN and GREEN (1986) studied a parental Group III composition (Arakapas area) experimentally with particular attention to matching of observed phenocryst assemblages with phases crystallized under controlled pressure and temperature conditions. Conditions of magma segregation from residual harzburgite were determined as 1350°C, 8–9 kbar and the magma contained ~0.5–1 percent weight $H_2O$.

In Figure 11, we plot the Troodos Group III parental lava composition with derivative glasses and aphyric basalts to compare with the area of MORB glasses and the range of liquids derived from MORB pyrolite. The Troodos Group III parental liquid lies marginally outside (*i.e.*, is more refractory than) the olivine–control line from MORB pyrolite. In terms of phase relations a liquid close to Troodos Group III parental magma could be formed by melting of MORB pyrolite at the point of elimination of orthopyroxene from the residual phases, *i.e.*, a dunite residue. However, minor and trace element contents of the MORB–pyrolite derived melt do not match these of Troodos Upper Pillow Lava—a relation readily apparent in the first plagioclase to crystallize (~$An_{91}$ in Troodos UPL and ~$An_{78}$ in DSDP 3–18–7–1).

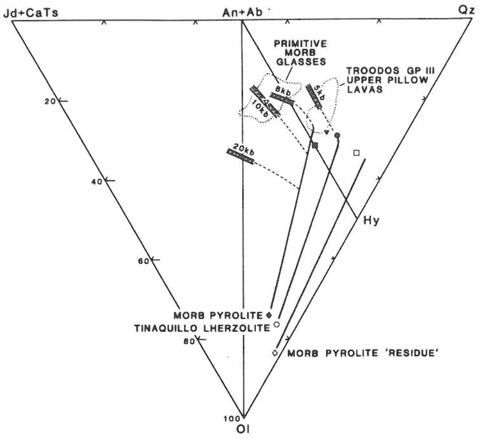

FIG. 11. Comparison of primitive MORB glasses and Troodos Group III upper pillow lavas (CAMERON, 1985) with equilibrium partial melts from 'MORB' pyrolite at 8, 10 and 20 kbar and Tinaquillo lherzolite at 5 kbar (JAQUES and GREEN, 1980; GREEN *et al.*, unpublished data), in the normative system Ol–Jd + CaTs–Qz–Di, projected from Di onto the plane Jd + CaTs–Qz–Ol. Cotectics same as for Figure 9. Symbols are as follows: (■) calculated parental composition for the Troodos Group III upper pillow lavas studied by DUNCAN and GREEN (1986). (▼) refractory primitive magma composition identified from glass inclusions in magnesian ($Fo_{94}$) olivine phenocrysts from Tonga (FALLOON and GREEN, 1986b). (●) Marianas fore-arc lava (JENNER, 1983). (□) Cape Vogel, boninite parental magma composition calculated by WALKER and CAMERON (1983). (▽) primitive MORB glass DSDP3–18–7–1 studied experimentally by GREEN *et al.* (1979).

If we compare the melting relations of Tinaquillo lherzolite (Figure 11), its more refractory character means that the olivine/orthopyroxene cotectic does not end at but continues through Troodos UPL composition (*cf.* Figure 1). In phase relations, trace element and minor element abundances, the source peridotite for Troodos UPL must be more refractory than MORB pyrolite—we infer that it is a residual lherzolite composition in which melting is enhanced by addition of a very small amount of water (0.5–1 percent weight $H_2O$ in the melt fraction) sufficient to depress the melting temperature by about 30–50°C.

### *Source for north Tongan arc high magnesium lavas*

In 1984, the Japanese research vessel 'Natsushima' dredged an extraordinary variety of high magnesium lavas from water depths in excess of 2000 m at the northern termination of the Tongan arc (FALLOON, 1985; FALLOON and GREEN, 1986a). In detail, the samples show evidence for decoupling of incompatible elements from major plus compatible elements. For example, rocks with similar major element chemistry have REE patterns varying from strongly LREE enriched to strongly LREE depleted. There is also unequivocal evidence for magma mixing involving several magnesian end-member liquids, differing principally in their degree of depletion in the more incompatible elements and in ratios such as Na/Ca. One sample contained $Fo_{94}$ olivine phenocrysts and within these unusually magnesian olivine crystals occur large glass inclusions with $CaO/Na_2O > 20$ and magnesian quartz tholeiite compositions (FALLOON and GREEN, 1986b). Correction for quench outgrowth on the olivine host enabled calculation of the original liquid (Figure 11). In other samples from the same and other dredge sites, extremely calcic plagioclase (up to $An_{100}$) megacrysts occur and are compatible with crystallization from a liquid matching the composition of the glass inclusions in olivine. The role of water in depressing the liquidus and fluxing melting of refractory lherzolite composition, is as yet uncertain. However, the composition of the glass inclusion is such that the original magma is a possible partial melt of very refractory lherzolite compositions, such as Tinaquillo lherzolite, with magma segregation at ~5 kbar (anhydrous) or a slightly higher pressure if $OH^-$ solution expands the olivine phase volume.

### *Source for boninite or high magnesia andesites*

In young West Pacific Arcs, distinctive very high $SiO_2$ (>56 weight percent, high magnesium, low calcium lavas characterized by rare olivine and abundant enstatite or multiply twinned clinoenstatite (inverted from protoenstatite) have been found both outcropping in emergent islands and dredged from the sea floor (DALLWITZ *et al.*, 1966; KURODA *et al.*, 1978; CRAWFORD *et al.*, 1981; UMINO, 1985; DIETRICH *et al.*, 1978). Strongly porphyritic character, accumulation of phenocrysts and growth of quench phases makes determination of liquid compositions very difficult. Experimental studies (TATSUMI, 1981; JENNER and GREEN, unpublished) have established conditions of multiple olivine and orthopyroxene saturation and the latter studies lead us to a preferred petrogenetic model in which liquids contain ~2 weight percent water and segregate from residual olivine and orthopyroxene at ~2–5 kbar, $T \sim$ 1250–1300°C.

In Figure 11, plots of possible parental magma compositions lie on the refractory (olivine–enstatite) side of the olivine-control line for peridotite such as MORB pyrolite or Tinaquillo lherzolite. Liquids such as boninites cannot be derived from lherzolites as calcic as those and require very refractory harzburgite source rocks (*cf.* Figure 1). Potential source rocks in terms of (Jd + CaTs)–Ol–Qz–Di include the more refractory compositions of the lherzolite-harzburgite suites of Figure 8. However, examination of trace element and minor element contents of boninites reveals great variability (JENNER 1981, HICKEY and FREY 1982, CAMERON *et al.*, 1983) from incompatible elements enriched to V–shaped REE patterns suggesting addition of a minor enriched component to a previously strongly depleted peridotite. A similar mechanism is required to explain the non–refractory character of the plagioclase (which appears very late in the crystallization sequence and lacks a high Ca/Na ratio). The geochemistry and petrology of boninites suggests volatile-induced ($H_2O$–rich) melting of very refractory residual harzburgite. There is evidence for significant addition of incompatible elements either with or prior to the addition of $H_2O$–rich fluid.

## CONCLUSIONS

The genesis of primary magmas in the earth's mantle is controlled by

a) Pressure, temperature variation, *i.e.*, mantle geotherms, which differ in different tectonic settings;
b) The presence and composition of a fluid phase, principally within the system C–H–O; and
c) The bulk compositions of source peridotite.

Experimental studies at high pressure and temperature constrain the effects of C–H–O fluid emphasizing the importance of water–rich and water–methane fluids at oxygen fugacities of IW to IW + 1 to 3 log units. The experimental studies also show that different source peridotite compositions are required for primary magmas from different tectonic settings. These different source compositions can be simply related within a framework in which the source compositions for Hawaiian (Hot–spot) and Mid–Ocean Ridge tholeiitic picrites to olivine tholeiites are regarded as 'enriched' and 'depleted' variants of the mantle composition within the asthenosphere. The process of enrichment and depletion is attributed to upward migration of a very small (~1%) melt fraction of olivine melilitite or olivine nephelinite character within the asthenosphere.

Source rocks for back–arc basin tholeiites, island arc tholeiites, high–Mg tholeiites such as Troodos Upper Pillow Lavas or from the Tongan fore–arc, and particularly for boninite parent magmas, are highly refractory lherzolites to harzburgites. The roles of such compositions as source rocks for magmas requires second and probably third stage melting, in which residues from extraction of earlier magmatic events are re–melted in different *P*, *T* and tectonic settings.

In such multiple melting episodes, a key role is played by C–H–O fluids in fluxing the melting, and in the case of boninite liquids, in introducing incompatible elements to the source rock prior to or during the melting process. Although the subducted slab has long been regarded as a source for $H_2O$–rich fluids by dehydration of minerals within the upper parts of the slab, in this paper we suggest that an additional source of water, particularly at deeper levels of the subduction process, comes from redox interaction of reduced $CH_4 + H_2$ fluids from the deep mantle with the oxidized (FMQ) mineral assemblages of the subducted slab.

Particularly favourable environments for multistage melting, even of extremely refractory harzburgite compositions within the subducted slab, occur at the intersections of subduction zones with transform faults, *e.g.*, northern end of Tongan Trench, southern end of Marianas Trench.

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## REFERENCES

ARCULUS R. J., DAWSON J. B., MITCHELL R. H., GUST D. A. and HOLMES R. D. (1984) Oxidation state of the upper mantle recorded by megacryst ilmenite in kimberlite and type A and B spinel lherzolite. *Contrib. Mineral. Petrol.* **85**, 85–94.

BASALTIC VOLCANISM STUDY PROJECT (1981) *Basaltic Volcanism on the Terrestrial Planets.* 1286 pp. Pergamon Press.

BOYD F. R. (1973) A pyroxene geotherm. *Geochim. Cosmochim. Acta* **37**, 2533–254.

BOYD F. R. and NIXON P. H. (1975) Origins of ultramafic rocks from some kimberites of northern Lesotho and the Monastery Mine, South Africa. *Phys. Chem. Earth* **9**, 431–454.

BREY G. P. and GREEN D. H. (1975) The role of $CO_2$ in the genesis of olivine melilitite. *Contrib. Mineral. Petrol.* **49**, 93–103.

BREY G. P. and GREEN D. H. (1976) Solubility of $CO_2$ in olivine melilitite at high pressures and role of $CO_2$ in the Earth's upper mantle. *Contrib. Mineral. Petrol.* **55**, 217–230.

BREY G. P., BRICE W. R., ELLIS D. J., GREEN D. H., HARRIS K. L. and RYABCHIKOV I. D. (1983) Pyroxene–carbonate reactions in the upper mantle. *Earth Planet. Sci. Lett.* **62**, 63–74.

BRYAN W. B. (1979) Regional variation and Petrogenesis of Basalt Glasses from the FAMOUS Area, Mid-Atlantic Ridge. *J. Petrol.* **20**, 293–325.

BYERS C. D., MUENOW D. W. and GARCIA M. D. (1983) Volatiles in basalts and andesites from the Galapagos Spreading Center, 85° to 86°W. *Geochim. Cosmochim. Acta* **47**, 1551–1558.

CAMERON W. E. (1985) Petrology and origin of primitive lavas from the Troodos ophiolite, Cyprus. *Contrib. Mineral. Petrol.* **89**, 239–255.

CAMERON W. E., MCCULLOCH M. R. and WALKER D. A. (1983) Boninite petrogenesis: chemical and Nd–Sr isotopic constraints. *Earth Planet. Sci. Lett.* **65**, 75–89.

CRAWFORD A. J., BECCALUVA A. L. and SERRI G. (1981) Tectonomagmatic evolution of the West Philippine-Mariana region and the origin of boninites. *Earth Planet. Sci. Lett.* **54**, 346–356.

DALLWITZ W. B., GREEN D. H. and THOMPSON J. E. (1966) Clinoenstatite in a volcanic rock from the Cape Vogel area, Papua. *J. Petrol.* **7**, 375–403.

DIETRICH V., EMMERMAN R., OBERHANSLI R. and PUCHELT H. (1978) Geochemistry of basaltic and gabbroic rocks from the West Mariana Basin and the Mariana Trench. *Earth Planet. Sci. Lett.* **39**, 127–144.

DUNCAN R. A. (1981) Hotspots in the Southern Oceans—An absolute frame of reference for motion of the Gondwana Continents. *Tectonophys.* **74**, 29–42.

DUNCAN R. A. and GREEN D. H. (1986) The genesis of refractory melts in the formation of oceanic crust. *Contrib. Mineral. Petrol.*, (Submitted).

EGGLER D. H. (1975) $CO_2$ as a volatile component of the mantle: The system $Mg_2SiO_4$–$SiO_2$–$H_2O$–$CO_2$. *Phys. Chem. Earth* **9**, 869–882.

EGGLER D. H. (1978) The effect of $CO_2$ upon partial melting of peridotite in the system $Na_2O$–$CaO$–$Al_2O_3$–$MgO$–$H_2O$–$CO_2$ to 35 kb, with an analysis of melting in a peridotite–$H_2O$–$CO_2$ system. *Amer. J. Sci.* **278**, 305–343.

EGGLER D. H. (1983) Upper mantle oxidation state: Evidence from olivine–orthopyroxene–ilmenite assemblages. *Geophys. Res. Lett.* **10**, 365–368.

EGGLER D. H. and BAKER D. R. (1982) Reduced volatiles in the system C–O–H: implications to meltings, fluid formation, and diamond genesis. In *High-Pressure Research in Geophysics,* (eds. S. AKIMOTO and M. MANGHNANI), pp. 237–250 Center for Academic Publications Japan, Tokyo.

FALLOON T. J. (1985) Preliminary petrography and geochemistry of igneous rocks from the Northern Tonga Ridge and adjacent Lau Basin. In *A Marine Geological and Geophysical Survey of the Northern Tonga Ridge and Adjacent Lau Basin,* (eds. E. HONZA, K. B. LEWIS *et al.*), pp. 63–71 Mineral Resources of Tonga Field Report No. 1, Ministry of Lands, Survey and National Resources, Kingdom of Tonga.

FALLOON T. J. and GREEN D. H. (1986a) Dredged igneous rocks from the Northern Termination of the Tofua Magmatic arc, Tonga and adjacent Lau Basin. *Australian Journal of Earth Sciences,* (Submitted).

FALLOON T. J. and GREEN D. H. (1986b) Glass inclusions in magnesian olivine phenocrysts from Tonga: Evidence for highly refractory parental magmas in the Tongan Arc. *Earth Planet. Sci. Lett.*, (In press).

FOLEY, S. F. (1986) The genesis of lamproitic magmas in a reduced fluorine-rich mantle. *Int. Kimb. Conf. Perth, Extended Abstracts 4th,* (In press).

FOLEY S. F., TAYLOR W. R. and GREEN D. H. (1986) The role of fluorine and oxygen fugacity in the genesis of the ultrapotassic rocks. *Contrib. Mineral. Petrol.*, (In press).

FREY F. A. and GREEN D. H. (1974) The mineralogy, geochemistry and origin of lherzolite inclusions in victorian basinites. *Geochim. Cosmochim. Acta* **38**, 1023–1059.

FREY F. A., GREEN D. H. and ROY D. S. (1978) Integrated models of basalt petrogenesis: a study of quartz tholeiites to olivine melilitites from south eastern Australia utilizing geochemical and experimental petrological data. *J. Petrol.* **19**, 463–513.

FREY F. S., SUEN J. C. and STOCKMAN H. W. (1985) The Ronda high temperature peridotite: Geochemistry and petrogenesis. *Geochim. Cosmochim. Acta* **49**, 2469–2491.

FROST B. R. (1979) Mineral equilibria involving mixed–

volatiles in a C–O–H fluid phase: the stabilities of graphite and siderite. *Amer. J. Sci.* **279,** 1033–1059.

Fujii T. and Scarfe C. M. (1985) Composition of liquids coexisting with spinel lherzolite at 10 kbar and the genesis of MORBS. *Contrib. Mineral. Petrol.* **90,** 18–28.

Gill J. B. (1981) *Orogenic Andesites and Plate Tectonics.* 390 pp. Springer-Verlag.

Gold T. and Soter S. (1980) The Deep–Earth–Gas hypothesis. *Sci. Amer.* **242,** 130–137.

Gold T. and Soter S. (1983) Methane and seismicity: a reply. *EOS* **64,** 663.

Green D. H. (1971) Composition of basaltic magmas as indicators of conditions of origin: application to oceanic volcanism. *Phil. Trans. Roy. Soc. London* **A268,** 707–725.

Green D. H. (1972) Magmatic activity as the major process in the chemical evolution of the earth's crust and mantle. *Tectonophys.* **13,** 47–71.

Green D. H. (1973) Experimental melting studies on a model upper mantle composition at high pressure under water–saturated and water–undersaturated conditions. *Earth Planet. Sci. Lett.* **19,** 37–53.

Green D. H. (1976) Experimental testing of equilibrium partial melting of peridotite under water–saturated, high-pressure conditions. *Can. Mineral.* **14,** 255–268.

Green D. H. and Ringwood A. E. (1967) The genesis of basaltic magmas. *Contrib. Mineral. Petrol.* **15,** 103–190.

Green D. H. and Liebermann R. C. (1976) Phase equilibria and elastic properties of the pyrolite model for the oceanic upper mantle. *Tectonophys.* **32,** 61–92.

Green D. H., Hibberson W. O. and Jaques A. L. (1979) Petrogenesis of mid–ocean ridge basalts. In *The Earth: Its Origin, Structure and Evolution,* (ed. M. W. McElhinny), pp. 265–299 Academic Press.

Green D. H., Taylor W. R. and Foley S. F. (1986) The Earth's upper mantle as a source for volatiles. *Geol. Soc. Aust. Special Pub. 12,* (In press).

Gupta A. K., Taylor W. R. and Green D. H. (1986) Experimental study of the system forsterite–nepheline–quartz at variable temperatures under 28 kb pressure, (Submitted).

Haggerty S. E. (1978) The redox state of planetary basalts. *Geophys. Res. Lett.* **5,** 443–446.

Hickey R. L. and Frey F. A. (1982) Geochemical characteristics of boninite series volcanics: implications for their source. *Geochim. Cosmochim. Acta* **46,** 2099–2115.

Hoffman A. W. and White W. M. (1982) Mantle plumes from ancient oceanic crust. *Earth Planet. Sci. Lett.* **57,** 421–436.

Holloway J. R. (1973) The system pargasite–$H_2O$–$CO_2$: a model for melting of a hydrous mineral with a mixed–volatile fluid—I. Experimental results to 8 kbar. *Geochim. Cosmochim. Acta* **37,** 651–666.

Jaques A. L. and Green D. H. (1980) Anhydrous melting of peridotite at 0–15 kb pressure and the genesis of tholeiitic basalts. *Contrib. Mineral. Petrol.* **73,** 287–310.

Jenner G. A. (1981) Geochemistry of high–Mg andesites from Cape Vogel, Papua New Guinea. *Chem. Geol.* **33,** 307–332.

Jenner G. A. (1983) Petrogenesis of high–Mg andesites: An experimental and geochemical study with emphasis on high–Mg andesite from Cape Vogel, P.N.G. Ph.D. Dissertation, Univ. of Tasmania.

Kurat G., Palme H., Spettel B., Baddenhausen H., Hofmeister H., Palme C. and Wanke H. (1980) Geochemistry of ultramafic xenoliths from Kapfenstein, Austria: evidence for a variety of upper mantle processes. *Geochim. Cosmochim. Acta* **44,** 45–60.

Kuroda N., Shiraki K. and Urano H. (1978) Boninite as a possible calc-alkaline primary magma. *Bull. Volcanol.* **41,** 563–575.

Kushiro I. (1968) Melting of a peridotite nodule at high pressures and high water pressures. *J. Geophys. Res.* **73,** 6023–6029.

Kushiro I. (1972) Effect of water on the compositions of magmas formed at high pressures. *J. Petrol.* **13,** 311–334.

Mathez E. A. (1984) Influence of degassing on oxidation states of basaltic magmas. *Nature* **310,** 371–375.

Mattioli G. S. and Wood B. J. (1986) Upper mantle $f_{O_2}$ recorded by spinel-lherzolites (abstr.) *EOS* **67,** 375.

McGetchin T. R., Silver L. T. and Chodos A. A. (1970) Titanoclinohumite: a possible mineralogical site for water in the upper mantle. *J. Geophys. Res.* **75,** 255–259.

Menzies M. (1983) Mantle ultramafic xenoliths in alkaline magmas: evidence for mantle heterogeneity modified by magmatic activity. In *Continental Basalts and Mantle Xenoliths,* (eds. C. J. Hawkesworth and M. J. Norry), pp. 92–110 Shiva Publ., Cheshire, England.

Morgan W. J. (1972) Plate motions and deep mantle convection. *Geol. Soc. Amer. Mem.* **132,** 7–22.

Mysen B. O. and Boettcher A. L. (1975) Melting of a hydrous mantle I. Phase relations of natural peridotite at high pressures and temperatures with controlled activities of water, carbon dioxide and hydrogen. *J. Petrol.* **16,** 520–548.

Mysen B. O. and Kushiro I. (1977) Compositional variations of coexisting phases with degree of melting of peridotite in the upper mantle. *Amer. Mineral.* **62,** 843–865.

Mysen B. O., Virgo D., Harrison W. J. and Scarfe C. M. (1980) Solubility mechanisms of $H_2O$ in silicate melts at high pressures and temperatures: A Raman spectroscopic study. *Amer. Mineral.* **65,** 900–914.

Nickel K. G. and Green D. H. (1984) The nature of the upper–most mantle beneath Victoria, Australia as deduced from ultramafic xenoliths. In *Kimberlites II: The Mantle and Crust-Mantle Relationships,* (ed. J. Kornprobst), pp. 161–178 Elsevier.

Nickel K. G. and Green D. H. (1985) Empirical geothermobarometry for garnet peridotites and implications for the nature of the lithosphere, kimberlites and diamonds. *Earth Planet. Sci. Lett.* **73,** 158–170.

Ringwood A. E. (1966) The chemical composition and origin of the earth. In *Advances in Earth Science,* (ed. P. M. Hurley), pp. 287–356 M.I.T. Press, Cambridge.

Ringwood A. E. (1974) The petrological evolution of island arc systems. *J. Geol. Soc. London.* **130,** 183–204.

Ringwood A. E. (1986) Dynamics of subducted lithosphere and implications for basalt genesis. *Terra Cognita* **6,** 67–77.

Ryabchikov I. D., Green D. H., Wall V. J. and Brey G. P. (1981) The oxidation state of carbon in the low-velocity zone. *Geochem. International* **18,** 148–158.

Sato M. (1978) Oxygen fugacity of basaltic magmas and the role of gas–forming elements. *Geophys. Res. Lett.* **5,** 447–449.

Sato M. and Valenza M. (1980) Oxygen fugacities of the layered series of the Skaergaard Instrusion, East Greenland. *Amer. J. Sci.* **20A,** 134–158.

Schairer J. F. and Yoder H. S. Jr. (1961) Crystallization in the system nepheline–forsterite–silica at one atmosphere pressure. *Carnegie Inst. Wash. Yearb.* **60,** 141–144.

STOLPER E. (1980) A Phase Diagram for Mid–ocean ridge basalts: Preliminary results and implications for petrogenesis. *Contrib. Mineral. Petrol.* **74,** 13–27.

TAKAHASHI E. and KUSHIRO I. (1983) Melting of a dry peridotite at high pressures and basalt magma genesis. *Amer. Mineral.* **68,** 859–879.

TATSUMI Y. (1981) Melting experiments on a high–magnesian andesite. *Earth Planet. Sci. Lett.* **54,** 357–365.

TAYLOR W. R. (1985) The role of C–O–H fluids in upper mantle processes: a theoretical, experimental and spectroscopic study. Ph.D. Dissertation, Univ. of Tasmania.

TAYLOR W. R. (1986) A reappraisal of the nature of fluids included by diamond—a window to deep-seated mantle fluids and redox conditions. *Geol. Soc. Aust. Special Publ.* **12,** (In press).

TAYLOR W. R. and GREEN D. H. (1987) The petrogenic role of methane: Effects on liquidus phase relations and the solubility of reduced C–H–O volatiles. In *Magmatic Processes: Physicochemical Principles,* (ed. B. O. MYSEN), pp. 121–138 The Geochemical Society Spec. Publ. No. 1.

UMINO S. (1985) Volcanic geology of Chichijima, the Bonin Islands. *J. Geol. Soc. Japan* **91,** 505–523.

WALKER D. A. and CAMERON W. E. (1983) Boninite primary magmas: evidence from the Cape Vogel Peninsula, P.N.G. *Contrib. Mineral. Petrol.* **83,** 150–158.

WEDEPOHL K. H. (1985) Origin of the Tertiary basaltic volcanism in the northern Hessian Depression. *Contrib. Mineral. Petrol.* **89,** 122–145.

WELHAN J. A. and CRAIG H. (1979) Methane and hydrogen in East Pacific Rise hydrothermal fluids. *Geophys. Res. Lett.* **6,** 829–831.

WELHAN J. A. and CRAIG H. (1983) Methane, hydrogen and helium in hydrothermal fluids at 21°N on the East Pacific Rise. In *Hydrothermal Processes at Seafloor Spreading Centres,* (eds. P. A. RONA, K. BOSTROM, L. LAUBIER and K. L. SMITH), pp. 391–409 Plenum Press, New York.

WENDLANDT R. F. and MYSEN B. O. (1980) Melting phase relations of natural peridotite + $CO_2$ as a function of degree of melting at 15 and 30 kbar. *Amer. Mineral.* **65,** 37–44.

WINDOM K. E. and BOETTCHER A. L. (1981) Phase relations for the joins jadeite–enstatite and jadeite–forsterite at 28 kb and their bearing on basalt genesis. *Amer. J. Sci.* **281,** 335–351.

WOERMANN E. and ROSENHAUER M. (1985) Fluid phases and the redox state of the Earth's mantle: extrapolations based on experimental, phase–theoretical and petrological data. *Fortschr. Mineral.* **63,** 263–349.

WYLLIE P. J. (1978) Mantle fluid compositions buffered in peridotite-$CO_2$–$H_2O$ by carbonates, amphibole, phlogopite. *J. Geology* **86,** 687–713.

WYLLIE P. J. (1979) Magmas and volatile components. *Amer. Mineral.* **65,** 469–500.

WYLLIE P. J. (1980) The origin of kimberlites. *J. Geophys. Res.* **85,** 6902–6910.

YODER H. S. JR. and TILLEY C. E. (1962) Origin of basalt magmas: an experimental study of natural and synthetic rock systems. *J. Petrol.* **3,** 342–532.