The role of oxidation-reduction and C–H–O fluids in determining melting conditions and magma compositions in the upper mantle

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Abstract. High pressure experimental studies of the melting of lherzolitic upper mantle in the absence of carbon and hydrogen have shown that the lherzolite solidus has a positive dP/dT and that the percentage melting increases quite rapidly above the solidus. In contrast, the presence of carbon and hydrogen in the mantle results in a region of 'incipient' melting at temperatures below the C, H-free solidus. In this region the presence or absence of melt and the composition of the melt are dependent on the amount and nature of volatiles, particularly the CO_2 , H_2O , and CH_4 contents of the potential C–H–O fluid. Under conditions of low f_{O_2} (IW to IW + 1 log unit at $P \sim 20\text{--}35\text{ kb}$), fluids such as $\text{CH}_4 + \text{H}_2\text{O}$ and $\text{CH}_4 + \text{H}_2$ inhibit melting, having a low solubility in silicate melts. Under these conditions, carbon and hydrogen are mobile elements in the upper mantle. At slightly higher oxygen fugacity (IW + 2 log units, $P \sim 20\text{--}35\text{ kb}$) fluids in equilibrium with graphite or diamond in peridotite C–H–O are extremely water-rich. Carbon is thus not mobile in the mantle in this f_{O_2} range and the melting and phase relations for the upper mantle lherzolite approximate closely to the peridotite– H_2O system. Pargasitic amphibole is stable to solidus temperatures in fertile lherzolite compositions and causes a distinctive peridotite solidus, the 'dehydration solidus', with a marked change in slope (a 'back bend') at 29–30 kb due to instability of pargasite at high pressure. Intersections of geothermal gradients with the peridotite– H_2O solidi define the boundary between lithosphere (subsolidus) and asthenosphere (incipient melt region). This boundary is thus sensitive to changes in f_{O_2} [affecting $\text{CH}_4\text{:H}_2\text{O:CO}_2$ ratios] and to the amount of H_2O and carbon (CO_2 , CH_4) present. At higher f_{O_2} conditions (IW + 3 log units), CO_2 -rich fluids occur at low pressures but there is a marked depression of the solidus at 20–21 kb due to intersection with the carbonation reaction, producing the low temperature solidus for dolomite amphibole lherzolite ($T \sim 925^\circ\text{C}$, 21 to $> 31\text{ kb}$). Melting of dolomite (or magnesite) amphibole lherzolite yields primary sodic dolomitic carbonatite melt with low H_2O content, in equilibrium with amphibole garnet lherzolite.

The complexity of melting in peridotite–C–H–O provides possible explanations for a wide range of observations on lithosphere/asthenosphere relations, on mantle melt and fluid compositions, and on processes of mantle metasomatism and magma genesis in the upper mantle.

Keywords. Oxidation-reduction; C–H–O fluids; melting conditions; magma composition; upper mantle; peridotite melting; reduced solidus; water-maximum solidus; oxidized solidus.

1. Introduction

A major activity of experimental petrology in recent years has been to investigate the controls by pressure, temperature and source peridotite composition in determining the compositions of primary magmas from the earth's upper mantle. The problem to be investigated is the petrogenesis of high-magnesia liquids as diverse as boninites with $> 55\%$ SiO_2 to olivine melilitites (35% SiO_2), kimberlites and possibly carbonatites ($< 5\%$ SiO_2). The elements carbon and hydrogen play an important role in petrogenesis – they are assumed to be important components in the earliest condensation of the solar system but estimates of their abundances in the deep earth

Figure 1. Compositions of fluid phase in equilibrium with graphite at $T = 1600\text{ K}$, $P = 30\text{ kbar}$ (Taylor and Green 1989).

are model-dependent. Observations on volcanic eruptions and from fluid inclusions and mineralogy in deep crust and upper mantle rock samples, confirm that carbon and hydrogen are the most important of the volatile elements (apart from oxygen) although sulphur, nitrogen, fluorine and chlorine may have significant roles in some processes.

The roles of carbon and hydrogen in magma genesis are strongly dependent on the mantle oxidation state i.e. activity of oxygen in the mantle environment. This is illustrated in figure 1 (Taylor and Green 1989) in which the carbon (graphite/diamond) saturation curve is plotted as a function of $C/C + H$ ratio and $\log f_{O_2}$.

The stability field of the involatile solid phase, graphite or diamond, extends to very water-rich ($> 90\text{ mol}\%$ H_2O) fluids at $f_{O_2} \sim \text{IW} + 2\text{ log units}$ [IW is iron-wustite] at high pressures and divides the C–H–O system into an oxidized fluid field ($\text{H}_2\text{O} + \text{CO}_2$) at $f_{O_2} > \text{CCO}$ [graphite–CO–CO₂] (near $\text{IW} + 3\text{ log units}$) and a reduced fluid field ($\text{H}_2\text{O} + \text{CH}_4 + \text{H}_2$) at $f_{O_2} < \text{IW} + 1\text{ log units}$. Naturally the mineral phases of the upper mantle will also reflect ambient f_{O_2} conditions—an oxidized upper mantle approaching FMQ (fayalite-magnetite-quartz) would be expected to show high Fe^{3+} contents in spinel, garnet or clinopyroxene, whereas at IW conditions, Fe^{3+} would not be expected in solid solutions of the major phases, and reduced Cr (Cr^{2+}) and titanium (Ti^{3+}) may be observed. More importantly metallic nickel, rather than Ni^{2+} solid solution in olivine, may appear at very low oxygen activities in the upper mantle.

It is an open question whether the mineral phases of the earth's upper mantle determine the oxidation state and thus the speciation of any C–H–O fluid which may be locally present, or whether a flux of migratory C–H–O fluid has a major role in determining the oxidation state of the Earth's upper mantle. In either case, experimental petrology has a role to play, i.e. to determine the nature of the interactions between oxidized and reduced C–H–O fluids and upper mantle mineralogy, using the techniques of high-pressure and high temperature experiment.

2. Peridotite melting—the C,H-free solidus

The melting behaviour of lherzolitic upper mantle, in the absence of carbon and hydrogen, is determined by multi-phase cotectic and solid solution melting relations among the minerals olivine, orthopyroxene, clinopyroxene, garnet, spinel and plagioclase. In the absence of solid solution in the major minerals, melting of such multiphase assemblages would be dominated by eutectoid melting and % melt vs T curves would be expected to have a stepped nature. Melting dominated by solid solution has linear or curvilinear % melt vs T curves. Experimental studies of C,H-free lherzolite compositions have demonstrated that solid solution effects are dominant with % melt vs T curves being linear or curvilinear, at least for moderate degrees of melting ($> 10\%$) (Jaques and Green 1980; Falloon and Green 1987, 1988; McKenzie and Bickle 1988). In C,H-free lherzolite the amount of melt present increases quite rapidly above the solidus, e.g. 30% melt is present within 150°C of the solidus for a fertile lherzolite (Hawaiian pyrolite) and within 180°C of the solidus for a more refractory lherzolite (Tinaquillo lherzolite) (Jaques and Green 1980). The solidus has a positive dP/dT to pressures of at least 50 kb (Jaques and Green 1980; Takahashi 1986).

The C,H-free solidi for model upper mantle lherzolite compositions are of limited value when considering the real mantle solidus or when considering very small degrees of melting. This is because very small amounts of volatile components, particularly C-H-O fluids but also including F, Cl and S as volatile 'trace' or 'minor' elements in the mantle, have a profound effect in fluxing melting or lowering the solidus. These elements are highly concentrated in the melt fraction, e.g. 0.05% H_2O in a source lherzolite will be concentrated as 5% H_2O in a 1% melt fraction of garnet lherzolite at 30 kb. (The melt will be of olivine nephelinite character with liquidus at $\sim 1300^\circ\text{C}$ at 30 kb—Green 1973). However at 25% melting of the source lherzolite, water content of the melt will be 0.2%, a similar value to water contents of olivine tholeiitic magmas of mid-ocean ridge or ocean island occurrence. Low water contents of $< 0.5\%$ have little effect on liquidus phase relationships apart from small depression of liquidus temperatures so that the results of C,H-free melting studies of lherzolite remain applicable in a quantitative way to our analysis of melting in peridotite-C-H-O *provided that* we are considering products and characteristics of higher degrees of melting ($> 10\%$ approx.) and that the C,H contents of the source lherzolite are very low.

It is possible to consider the melting behaviour of mantle lherzolite as two distinctive regimes. The higher temperature regime is bounded by the C,H-free solidus, above which melting increases relatively rapidly and melt compositions are determined by melting and phase relations among major mantle minerals. The lower temperature regime lies between the C,H-free solidus and the appropriate peridotite-C-H-O solidus (refer later sections and figures 3, 5). In this regime the amount and character of the volatile components dominates the melting process, % melting increases slowly with increasing temperature and melt compositions are highly enriched in incompatible elements (i.e. those elements partitioned into liquid relative to the residual minerals present). This region may be called the region of incipient melting in contrast to the higher temperature regime of major melting. Most geophysical models of mantle melting, particularly those emphasizing melting by convective upwelling in mid-ocean ridge or hot-spot location, have used the C,H-free

solidi and, as a first approximation, neglected the important incipient melting regime resulting from C–H–O volatile (+ Cl, F, S) contents of the upper mantle. The distinction between ‘incipient’ and ‘major’ melting regimes breaks down if high contents of C–H–O fluids are present or introduced into the upper mantle (refer discussion of peridotite–H₂O in convergent margin environments)—under these conditions high degrees of melting (‘major’ melting) occur at temperatures well below the C,H-free peridotite solidus.

3. Peridotite–CH₄–H₂O: The ‘reduced’ solidus

Although it is not possible as yet to unequivocally determine the oxidation state of the earth’s upper mantle, estimates range from oxygen fugacity conditions near fayalite-magnetite-quartz to a lower limit close to iron-wustite. In the lower part of this range, CH₄ and H₂O are the dominant volatiles in the C–H–O system (figure 1). Although H₂O reacts with mantle silicates to form hydrated phases such as amphibole, phlogopite, talc etc. under appropriate *P*, *T* conditions, methane is unreactive and in addition has a low solubility in silicate melts (Taylor and Green 1987). An experimental study (Taylor and Green 1988) used a double-capsule buffering technique and techniques of fluid-analysis by the piercing of quenched capsules, to study the melting and phase relationships of peridotite–CH₄–H₂O to pressures of 35 kb. A fluid was present in all experiments and oxygen fugacity conditions were maintained at close to (IW + 1 log unit) using a tungsten carbide-tungsten oxide buffer.

Under subsolidus conditions, methane-water fluids co-exist with spinel + amphibole lherzolite mineral assemblages at low pressure (< 18 kb at 1100°C), with garnet + amphibole lherzolite assemblages from 18 to 30 kb at 1100°C and with garnet + phlogopite lherzolite assemblages above 30 kb. Although the presence of methane has little effect on the stability of pargasitic amphibole, which persists up to 1170°C at 20 kb, it has a marked effect in raising the solidus temperature to temperatures well above those of the fluid-saturated system with water only (i.e. peridotite–H₂O, without carbon). It has been possible to use the experimentally determined solidus for WC–WO-buffered C–H–O fluids and the analysed compositions of fluids, to estimate the positions of the (CH₄ + H₂O), fluid-saturated, solidus for mantle peridotite to depths in excess of 100 km (figure 2). In this figure the solidi for various water activities are plotted, assuming a fluid of C–H–O composition (i.e. CH₄ and H₂O dominant species). At low pressures (< 15 kb), solidus depression by CH₄ + H₂O fluids is very large, even for CH₄-rich fluids. However, at higher pressures, even relatively small CH₄-contents in the fluid phase caused marked increase in solidus temperature relative to that in the peridotite–H₂O system. Thus at higher pressures, the presence of CH₄ in the fluid phase inhibits melting and raises the mantle solidus temperature towards the dry (C–H-free) solidus. The effect of this, in terms of models of melting of the upper mantle, is illustrated in figure 2, where a model continental geotherm, applicable to areas beneath ancient continental shields, only intersects the peridotite–H₂O (*a*_{H₂O} = 1) solidus and does not intersect the solidi for peridotite–CH₄–H₂O, even for *a*_{H₂O} ~ 0.85.

From this experimental study we may infer that if mantle *f*_{O₂} conditions are near

Figure 2. P , T projection of the P - T - $a\text{H}_2\text{O}$ solidi for the system peridotite- CH_4 - H_2O (graphite/diamond present). Solidi for water activities of ~ 0 , 0.35, 0.70, 0.85 and the water maximum (see figure 1) are shown. CG—Continental shield geotherm; PG—thermally perturbed geotherm beneath shield regions; SEAG—southeastern Australian geotherm; G—graphite; D—diamond. Light dashed curve is the pargasite stability limit for $a\text{H}_2\text{O} \sim 0.5$.

IW + 1 log unit and both carbon and hydrogen are present as minor or trace components in the upper mantle, then CH_4 -rich or $\text{CH}_4 + \text{H}_2\text{O}$ fluids will be very mobile and coexist in equilibrium with phlogopite-garnet lherzolite or amphibole garnet lherzolite. Carbon is thus readily mobile. However, such fluids are sensitive to change of ambient f_{O_2} conditions and if they migrate to a region of higher f_{O_2} (e.g. IW + 2 log units) then carbon will precipitate from the fluid phase (as diamond or graphite depending on the P , T conditions) which will become more water-rich. The change of fluid to higher $a_{\text{H}_2\text{O}}$ may cause melting if the ambient P , T conditions are above the peridotite- H_2O solidus. This process has been called 'redox melting' (Green *et al* 1987; Taylor and Green 1989). Melting is initiated at a given P , T condition without any change in P and T but simply by interaction between a higher f_{O_2} mineral assemblage and a reduced $\text{CH}_4 + \text{H}_2\text{O}$ fluid. A similar 'redox melting' reaction occurs if oxidized H_2O (+ CO_2)-fluid enters a peridotite region with low f_{O_2} conditions.

The importance of redox melting in upper mantle petrogenesis may be restricted by the limited oxygen buffering capacity of mantle lherzolite assemblages. As an approximation, a mantle lherzolite containing 1% Fe_2O_3 (in garnet, spinel, clinopyroxene, orthopyroxene) which is reduced to FeO by interaction with 0.11 wt% of mantle-derived fluid (50:50 = CH_4 : H_2O) will produce (at ~ 35 kb, 1100°) approximately 1% melt containing $\sim 17\%$ H_2O . The melt will be very silica-undersaturated and of olivine-rich nephelinitic or olivine leucite composition, containing very low dissolved carbonate (CO_3^{2-}) contents (at IW + 2 log units). This example of redox interaction of 'oxidized' mantle lithosphere with reduced $\text{CH}_4 + \text{H}_2\text{O}$ fluid would precipitate 0.04% carbon (diamond or graphite) as a corollary to the production of 1% melt.

4. Peridotite-H₂O: The water-maximum solidus

If mantle f_{O_2} conditions at pressures of 30 kb or more are close to IW + 2 log units, then fluids in the C-H-O system will be > 90 mol% H₂O (figure 1) with only very small CO₂ and CH₄ contents in the fluid phase. The peridotite-C-H-O system will approximate to the peridotite-H₂O system with the presence of carbon having minimal effects on phase relationships, melt compositions or melting temperatures.

The system peridotite-H₂O has been studied experimentally at low oxygen fugacity conditions and a major feature of this system is the stability field for pargasitic amphibole. Pargasitic amphibole, particularly Ti-bearing pargasite, is stable in peridotitic compositions to above 1150°C at 15–25 kb, but is restricted to depths in the upper mantle of less than about 90 km. At higher pressures pargasite breaks down to olivine + pyroxenes + garnet + phlogopite + ilmenite, i.e. a mineral assemblage containing much less than the 1.5 wt% H₂O approx. retained by pargasitic amphibole. Thus a fertile lherzolite composition (i.e. with 3–4% CaO, Al₂O₃, > 0.3% Na₂O, > 0.3% TiO₂ approx.) will crystallize up to 30 wt% pargasitic amphibole at pressures up to 30 kb and temperatures to ~1150°C. Pargasite-bearing lherzolite may thus contain 0.4 wt% H₂O with no fluid phase within the pargasite stability field but at pressures of 31 kb, $T \sim 1050^\circ\text{C}$ (i.e. at pressures greater than the amphibole stability limit) such a lherzolite composition would be represented by phlogopite, garnet lherzolite with ~1% melt (containing ~30 wt% H₂O) and a water-rich vapour. The melt would be extremely undersaturated olivine nephelinitic to melilititic melt and the solubility of carbon (as carbonate principally) would be sensitive to very small changes in f_{O_2} and the presence or absence of graphite or diamond as an additional trace phase in the lherzolite composition.

The peridotite-H₂O phase diagram is of fundamental importance to discussions of mantle melting and to lithosphere-asthenosphere characteristics. In figure 3, estimated geothermal gradients for stable continental shield regions and mature oceanic crust are shown in relation to the solidi for a fertile lherzolite (carbon-free) composition under anhydrous, water-saturated and water-undersaturated (at $P < 30$ kb, i.e. < 0.4% H₂O approx.) conditions. The intersection of the regional geothermal gradient with an appropriate solidus will correspond to a marked change in mechanical properties of the upper mantle lherzolite. It is suggested that sub-solidus conditions characterize the lithosphere, and the asthenosphere contains a small interstitial melt fraction. If this distinction between solid lithosphere and partially molten asthenosphere is accepted as a working hypothesis, then the results of experimental study of the peridotite-H₂O system place the lithosphere/asthenosphere boundary at 85–90 km depth in regions of mature oceanic crust (i.e. H₂O contents < 0.4% H₂O in lithospheric peridotite) but at ~60 km depth in the mantle wedge overlying Benioff Zones (i.e. H₂O contents > 0.4% because of water-rich fluid migration from subducted lithospheric slabs). A very low geothermal gradient beneath ancient continental shield regions (figure 3) may not intersect the peridotite-H₂O solidus, at least at depths < 150 km—the lithosphere would extend to at least this depth and a region of partial melting may be absent.

The distinctive shape of the peridotite-H₂O solidus, particularly for small water contents, is a consequence of the role of pargasitic amphibole and its stability up to solidus temperatures (the 'dehydration solidus' of figure 3, solidus 2).

Models for the upper mantle based on the phase relationships summarized in

Figure 3. Solidi (heavy lines) for Hawaiian pyrolite without C, H(1) with excess H_2O (4) and for the special case (2) where fluid is absent and H_2O is present in pargasitic amphibole (< 30 kb) – i.e. the pargasite dehydration solidus. Similar solidi are sketched for crustal melting—light lines 1–4 in the pressure range to 15 kb. The diagram also shows estimates of the geothermal gradient beneath 100 myr old oceanic crust ($P\text{-}O_{100}$) and beneath ancient shield regions (CR Shield). PJ is an estimate for the P – T path of an adiabatically upwelling mantle convective system meeting a boundary layer (?lithosphere) at ~ 100 km. The figure provides a conceptual framework for petrogenesis of anhydrous and hydrous silicate melts and lithosphere (sub-solidus) vs asthenosphere (small or incipient melt) contrasts in different thermal regimes.

figure 3 have been presented previously (Green 1971, 1972, 1973; Green and Liebermann 1976). More recent work [Green *et al* 1988; Mengel and Green 1989; Niida and Green (in prep.)] has confirmed the pattern of pargasitic amphibole stability in fertile lherzolite compositions but reveals a paradox in that the dehydration solidus in more 'refractory' lherzolite compositions (i.e. with lower TiO_2 , K_2O and Na_2O contents) is at a lower temperature than the solidus for 'enriched'

lherzolite compositions [Green *et al* 1988; Niida and Green (in prep.)]. The major conclusion however, is that pargasitic amphibole has an important role in the lithosphere as a minor phase or major phase retaining water and incompatible elements in subsolidus assemblages to depths of 85–90 km.

The lithosphere/asthenosphere boundary, assuming that this is determined by the mantle solidus, is sensitively dependent on the geothermal gradient and on the presence or absence of water. The role of water must be considered within the C–H–O system and thus the discussion and mantle model presented in this section is relevant to mantle compositions without carbon (possibly an unrealistic situation) or, more importantly, to peridotite–C–H–O with f_{O_2} conditions at $P > 30$ kb approx. close to $IW + 2 \log$ units, i.e. on the ‘water maximum’ of figure 1. Referring back to the earlier discussion, any reduction process, e.g. by access of CH_4 -rich fluid from deeper in the mantle, will inhibit melting and may ‘freeze’ an asthenospheric layer to garnet-phlogopite-lherzolite (+ graphite/diamond) with $CH_4 + H_2O$ fluid. Conversely an oxidation process, e.g. by migration of $(H_2O + CO_2)$ fluids from a subducting slab, will modify melting relations from the peridotite– H_2O system to peridotite– H_2O – CO_2 .

5. Peridotite– H_2O – CO_2 : The ‘oxidized’ solidus

At higher oxygen fugacities (figure 1) the mantle may contain graphite (diamond) + $(H_2O + CO_2)$ fluid, graphite + carbonate + hydrous silicate phases or graphite (diamond) may be absent (higher oxygen fugacities). The nature of subsolidus and melting relations of the mantle are thus made more complex by the stability of carbonates (dolomite, magnesite) under upper mantle conditions and by the pressure/temperature dependent solubility of $CO_2(CO_3^{2-})$ in silicate melts.

The decarbonation reaction (1):

divides the subsolidus lherzolite P , T field into a lower pressure, higher temperature regime in which $CO_2 + H_2O$ fluids coexist with spinel or plagioclase lherzolite mineralogy in which the stability of pargasitic amphibole ($\pm$ phlogopite) and the solidus temperature are determined by the $H_2O:CO_2$ ratio. The P , T conditions for the carbonation reaction (1) are also sensitive to $H_2O:CO_2$ and the reaction is displaced to higher pressures with higher $H_2O:CO_2$ ratio.

At pressures greater than reaction (1), carbonate is stable in subsolidus peridotite and coexists with hydrous phases (pargasite, $\pm$ phlogopite) and H_2O -rich fluid. At low $CO_2 + H_2O$ contents, a fluid-absent dolomite + pargasite + garnet lherzolite assemblage occurs. The solidus of this assemblage, i.e. garnet lherzolite containing both dolomite and pargasite, is at $\sim 925^\circ\text{C}$ from near 23 kb to at least 33 kb (Wallace and Green 1988; Falloon and Green 1990) and is at 50 to 100°C below the water-saturated peridotite– H_2O solidus. The nature of the melt at the solidus at $P > 21$ kb is a sodic dolomitic carbonatite with $\sim 3\%$ SiO_2 and even under fluid-saturated conditions and coexisting with pargasite, the carbonatite melt contains a low water content ($1 \sim 2\%$ H_2O) (Wallace and Green 1988).

The melting behaviour in peridotite– CO_2 – H_2O will vary depending on whether there is more H_2O than can be held in pargasite and also on the $H_2O:CO_2$ ratio (at

Figure 4. Phase relations for Hawaiian pyrolite plus added H_2O , CO_2 volatiles. A is Hawaiian pyrolite- $\text{H}_2\text{O}_{\text{saturated}}$ (Green 1973a); B is Hawaiian pyrolite- $\text{H}_2\text{O}-\text{CO}_2$ (Falloon and Green 1990); C is Hawaiian pyrolite- $\text{H}_2\text{O}-\text{CO}_2$ (in part fluid-absent) (Wallace and Green 1988); D is Hawaiian pyrolite- CO_2 (Falloon and Green 1989). I_6 , Q , Q' are intersections of decarbonation reaction (1) with pyrolite solidus. Dashed line is amphibole breakdown reaction. Solid lines with tick marks are vapour-free solidi. Number reaction curves are as follows: (1) decarbonation reaction forsterite + diopside + $\text{CO}_2 \leftrightarrow$ enstatite + dolomite; (2) reaction enstatite + dolomite $\leftrightarrow$ diopside + magnesite.

pressures below the intersection of reaction (1) with the solidus). At pressures above the intersection of reaction (1) with the solidus, if fluid is present (i.e. $\text{H}_2\text{O} > 0.4\%$ approx.), it will be water-rich and of a fixed composition independent of the bulk $\text{H}_2\text{O}:\text{CO}_2$ ratio—a 'zone of invariant vapour composition' (ZIVC; Eggler 1978).

In figure 4, four different solidi in peridotite- $\text{H}_2\text{O}-\text{CO}_2$ are compared and are superimposed in figure 5 (Wallace and Green 1988; Green and Wallace 1988; Falloon and Green 1989, 1990). Important features of the figures include the vapour-absent solidi at $P > 20$ kb for peridotite- CO_2 and between 21 kb and 31 kb for peridotite- $\text{H}_2\text{O}-\text{CO}_2$ ($\text{H}_2\text{O} < 0.4 \text{ wt}\%$). Carbonatite melts are present in the pargasitic amphibole stability field, with or without H_2O -rich fluid. Silicate melts, with dissolved CO_3^{2-} , occur at temperatures above amphibole breakdown (up to 30 kb). At pressures greater than 30 kb pargasitic amphibole is not stable and an extensive P, T field of carbonatite melt in equilibrium with garnet lherzolite occurs at temperatures below the water-saturated solidus, i.e. at 35 kb, over a temperature interval from 930 to $\sim 1080^\circ\text{C}$. At higher temperatures it is expected that carbonatite melts will dissolve in the more voluminous silicate melts which have a high solubility for CO_3^{2-} —this will occur at temperatures near and above the peridotite- H_2O solidus.

Referring to figure 5, it is apparent that the estimated continental shield geotherms, which do not intersect the peridotite- H_2O solidus (figure 3 and curve A, figure 5), do intersect the peridotite + $\text{H}_2\text{O} + \text{CO}_2$ solidus at $P > 31$ kb, $T \sim 930^\circ\text{C}$. The oceanic geotherm traverses a field of carbonatite melt coexisting with pargasite lherzolite before entering a field of carbonated silicate melt + lherzolite residue at higher

Figure 5. Solidi for pyrolite C-H-O (see below) and relationships to estimated geothermal gradients of oceanic or shield type. Area with horizontal pattern: P, T conditions at which a carbonatite melt occurs at temperatures below the water-saturated pyrolite solidus. Area with vertical pattern: P, T conditions at which a carbonatite melt may coexist with an H_2O -rich fluid and a residual pargasite lherzolite.

F = Solidus for Hawaiian pyrolite (C,H-absent)

A = Solidus for Hawaiian pyrolite + H_2O (excess H_2O , i.e. $> 0.4\%$ H_2O approx.)

A' = Solidus for Hawaiian pyrolite + H_2O ($< 0.4\%$ H_2O) (coincides with amphibole-out at solidus up to 30 kb)

B = Solidus for Hawaiian pyrolite + H_2O + CO_2 with excess fluid, i.e. $H_2O \sim 2\%$, $CO_2 \sim 2\%$ (Falloon and Green, 1990)

D = Solidus for Hawaiian pyrolite + CO_2 (2.4 wt%)

E = Solidus for Hawaiian pyrolite + H_2O + CH_4 (H_2O + CH_4 fluid buffered by WO-WC buffer).

Reactions (1) and (2) as in figure 4. I_6-Q' – migration of intersection of decarbonation reaction 1 with solidus as a function of increasing $H_2O:CO_2$ ($I_6 \rightarrow Q'$).

pressures. The demonstration that primary sodic dolomitic carbonatite melts coexist with pargasite-bearing garnet lherzolite is an important factor in the consideration of melt and fluid migration in the upper mantle and consequent mantle metasomatism. Mantle metasomatism (and variations in trace element and isotopic compositions of mantle-derived magmas) is principally concerned with the variation in incompatible element concentrations, separation of large ion lithophile elements (LILE) from high field strength elements (HFSE) and fractionation among similar elements, e.g. REE, HFSE. In the coexistence of carbonatite melt and pargasitic amphibole it is clear that phosphorus, for example, partitions into the melt but titanium is 'refractory' in pargasite. LILE and LREE elements similarly would partition into the carbonatitic melt but HFSE would reside in amphibole.

Speculations on the nature of metasomatism and metasomatic products in the 'oxidized' mantle at pressures > 20 kb must consider potential roles for H_2O -rich

fluid at conditions below solidus *B* (figure 5), carbonatite melt $\pm$ H₂O-rich fluid at conditions between solidi *A* and *B* and carbonated silicate melt $\pm$ immiscible carbonatite melt or carbonated silicate melt $\pm$ H₂O-rich fluid at conditions above solidus *A* (cf Green and Wallace 1988). Primary carbonatite melts are extremely reactive towards mantle lherzolite compositions at pressures < 21 kb approx. If a carbonatite magma should ascend to these pressures then it will react with orthopyroxene of the wall-rock lherzolite to form clinopyroxene + olivine and free CO₂-rich fluid inclusions. Examples of metasomatism of this character have been observed in suites of spinel lherzolite xenoliths from various locations (Green and Wallace 1988).

The experimental studies in the system peridotite-H₂O-CO₂ reveal a variety of processes by which very small melt fractions, strongly enriched in incompatible elements, may migrate at different levels of the lithosphere and asthenosphere. The metasomatic effects of movement of a small sodic dolomitic melt component, enriched in LILE, P, Na and Ca, are different from those of a small melilititic or nephelinitic silicate melt, enriched in LILE, HFSE, P, K and Na. The *P*, *T*-dependent stabilities of minerals such as amphibole, phlogopite and dolomite or magnesite will determine how these mobile, melt components react with and thus metasomatize regions of the upper mantle. In the lithosphere in within-plate areas, including the lithosphere beneath mature oceanic crust, it is probable that a region enriched in pargasitic amphibole may develop at depths of ~90 km due to the migration of a small, highly undersaturated silicate melt fraction (melilititic or nephelinitic) within the asthenosphere and the 'freezing' of this silicate melt as it enters the pargasitic amphibole stability field at pressures < 30 kb. This region of metasomatized mantle would have moderate LILE and high HFSE enrichment factors but any (CO₃²⁻) dissolved in the original melilititic or nephelinitic melt would not crystallize at ~90 km but instead form a sodic dolomitic carbonatite melt, highly enriched in LILE, P, Na and Ca. Migration of this carbonatitic melt to shallower levels in the lithosphere may cause a different type of metasomatism at depths of 55–65 km as the carbonatite melt reacts with orthopyroxene of mantle lherzolite to form clinopyroxene, apatite ($\pm$ pargasite, $\pm$ phlogopite) and olivine with CO₂-vapour, i.e. a metasomatic trend to convert lherzolite to wehrlite (Green and Wallace 1988). This distinctive metasomatism occurs in the spinel lherzolite stability field and results in enrichment of the upper part of the lithosphere in LILE, LREE, P, Na and Ca.

In convergent plate margin environments, the subduction of cool oceanic crust and lithosphere beneath a higher temperature mantle wedge of the overlying plate, creates an environment where the *P*, *T*, *f*_{O₂}-dependent melting relations of mantle lherzolite can produce distinctive enrichment and depletion processes in the mantle. It is assumed that the subducted crust and lithosphere is oxygen-rich, i.e. has high *f*_{O₂} from interaction with atmosphere and hydrosphere. The subduction process will result in dehydration and probably decarbonation reactions so that oxidized H₂O-rich or H₂O + CO₂ fluids may move from the subducted slab into the overlying mantle wedge. Various scenarios can be presented in which the stability of pargasitic amphibole, in equilibrium with a mobile, carbonatitic melt, causes separation of LILE and HFSE, the former becoming enriched in the mobile melt phase, the latter remaining fixed in residual amphibole. This therefore suggests that the mobility of carbonatitic melt within the mantle in the convergent margin environment may be the key mechanism for the enrichment of LILE, without concomitant enrichment in HFSE, in the source regions for island arc magmas.

6. Conclusions

Melting in the peridotite–C–H–O system is very sensitive to oxygen fugacity. In the Earth's upper mantle, estimates of ambient oxygen fugacity vary from FMQ to slightly greater than IW, i.e. > 4 orders of magnitude. However, the oxygen-buffering capacity of mantle lherzolites over this range of f_{O_2} is very limited and essentially restricted to $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$ variation and Fe_2O_3 solid solution in spinel, ilmenite, garnet, pyroxenes, amphibole and phlogopite. At low f_{O_2} values some reduction to Cr^{2+} and Ti^{3+} may also occur. Thus it is very likely that access of small amounts of reduced ($\text{CH}_4 + \text{H}_2\text{O}$) or oxidized ($\text{CO}_2 + \text{H}_2\text{O}$) fluids may rapidly change ambient mantle f_{O_2} conditions and conversely, mantle f_{O_2} variation may oxidize or reduce small amounts of C–H–O fluids if these are mobile under mantle conditions.

In the lithosphere and asthenosphere, to depths of ~ 150 km, relatively reduced conditions (IW + 1 log unit) produce $\text{CH}_4 + \text{H}_2\text{O}$ fluids, carbon is highly mobile in the fluid phase and melting is inhibited by the presence of CH_4 . At f_{O_2} near IW + 2 log units, graphite or diamond is stable with extremely water-rich fluid ($X_{\text{H}_2\text{O}} > 90$ mol%) and melting approximates to the peridotite– H_2O system. Near-solidus melts at $P > 20$ kb are very silica-undersaturated silicate melts which may have appreciable dissolved $(\text{CO}_3)^=$, particularly if f_{O_2} values approach those of the EMOG buffer (enstatite, magnesite, olivine, graphite).

At slightly higher f_{O_2} -values, the presence of C + H in the mantle results in the co-existence of dolomite or magnesite with pargasite-bearing garnet lherzolite and phlogopite garnet lherzolite, but only at pressures above the carbonation reaction (olivine + diopside + $\text{CO}_2 \leftrightarrow$ dolomite + enstatite). On the high pressure side of this reaction, melting of dolomite-pargasite lherzolite occurs at relatively low temperatures, about 50–70°C below the temperature of melting in the water-saturated peridotite– H_2O system. The melt phase is a sodic-dolomitic carbonatite which occurs in the P, T range 930–1080°C, 21–31 kb in lherzolite with $\sim 0.3\%$ H_2O , 0.5–2.5% CO_2 , in equilibrium with residual amphibole-garnet lherzolite. With higher water contents, a water-rich fluid is also present, both above and below the solidus. Carbonatitic melts may occur in the upper mantle at temperatures below those required for water-rich or ($\text{H}_2\text{O} + \text{CO}_2$)-rich silicate melts.

The peridotite–C–H–O melting relations are complex and offer reasonable, petrological constraints to models of asthenosphere and lithosphere and to models of petrogenesis of magmas, varying from carbonatites ($< 5\%$ SiO_2) to boninites ($> 55\%$ SiO_2).

Acknowledgements

This manuscript could not have been prepared without encouragement and patience from Dr Alok Gupta. Mr K Harris, Dr M Wallace, Dr T J Falloon and Dr W R Taylor are responsible for much of the published work on which this review is based. Mrs K Whelan and Mrs J Pongratz are thanked for preparing the manuscript and figures respectively. This paper is dedicated to the late Sir C V Raman, on the occasion of his birth centenary.

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