THE EFFECT OF H_2O AND CO_2 ON PLANETARY MANTLES

Peter J. Wyllie

Department of Geophysical Sciences, University of Chicago
Chicago, Illinois 60637

Abstract. The solidus for peridotite-H_2O-CO_2 is a divariant surface traversed by univariant lines that locate the intersections of subsolidus divariant surfaces for carbonation or hydration reactions occurring in the presence of H_2O-CO_2 mixtures. Vapor phase compositions are normally buffered to these lines; the buffering capacity of carbonates is much greater than that of amphibole and phlogopite. Near the buffered curve for the solidus of partly carbonated peridotite, extending to higher pressures and lower temperatures from an invariant point near 26 kb-1200°C, there is a temperature maximum on the peridotite-vapor solidus. On the CO_2 side of the maximum, above 26 kb, CO_2/H_2O is greater in liquid than in vapor, and liquids are SiO_2-poor; on the H_2O side of this maximum (including all pressures below 26 kb), H_2O/CO_2 is greater in liquid than in vapor, and liquids change from forsterite-normative to quartz-normative with increasing H_2O/CO_2 in vapor. Even traces of H_2O and CO_2, in minerals or vapor, lower mantle solidus temperatures through hundreds of degrees compared with the volatile-free solidus.

Introduction

Assuming that the compositions of planetary mantles correspond to peridotites, the effects of H_2O and CO_2 can be evaluated by extrapolation of published experimental data. Detailed review of sources, of selection of data, of controversies, and some justifications for extrapolations were given by *Wyllie* (1977) in his first treatment of the system peridotite-H_2O-CO_2. That review must be assumed in this brief Letter, which introduces some additional features for the phase diagram. Determination of the phase relationships in peridotite-H_2O-CO_2 is a first step for evaluation of the behavior of the components C-H-O in planetary mantles. The oxygen fugacity is a critical factor. The assumption that components C-H-O are present dominantly as H_2O and CO_2 is certainly not true for all mantles at all depths at all times.

H_2O and CO_2 may exist in minerals, in vapor phase, or in melts. The physical state and chemical behavior of volatile component-rich films in mantles needs evaluation; the solute content of H_2O-CO_2 fluid may reach tens of weight per cent. Amphibole, phlogopite, and carbonate can be crystalline hosts for H_2O and CO_2 at upper mantle pressures. Other possibilities, such as titanoclinohumite, dense hydrated magnesian silicates, and sanidine hydrate are neglected in this treatment. At temperatures above 800°C, many peridotites can be completely hydrated by about 0.4 wt. % H_2O, with formation of amphibole. At pressures above about 30 kbar, where amphibole is not stable, it requires only about 0.02 wt. % H_2O to produce maximum phlogopite in peridotite corresponding to the earth's mantle. In contrast, about 30 wt. % CO_2 is required to carbonate peridotite completely, producing an assemblage of carbonates + silica + aluminous mineral. There is a series of carbonation reactions, and a carbonate-pyroxene exchange reaction, in the pressure range up to 50 kbar.

The solubility of H_2O in silicate liquids increases to about 10 wt. % at 5 kbar and about 20 wt. % at 20 kbar. In contrast, the solubility of CO_2 in silicate liquids remains very low at pressures to 10 kbar, and reaches 1-4 wt. % (depending on liquid composition) at 20 kbar. In the pressure interval between about 20 and 26 kbar, however, the solubility of CO_2 in near-solidus liquids from peridotite increases dramatically to perhaps as much as 35-40 wt. %; this effect is associated with the subsolidus carbonation of peridotite, as discussed below.

For mantles with small amounts of H_2O and CO_2, only small amounts of liquid are developed below the solidus temperature of volatile-free peridotite. The compositions of the near-solidus liquids are influenced strongly by the proportions of CO_2 and H_2O, and the way they are distributed among vapor, carbonates, and hydrous minerals. Common basal-

tic liquids are developed at higher temperatures, nearer to the solidus for volatile-free peridotite, where H_2O and CO_2 are normally so diluted in the melt that they have little effect.

Peridotite-H_2O

The system was reviewed by *Wyllie* (1977). There are different results from different laboratories for the solidus and amphibole breakdown curves in different peridotites. Fig. 1 shows three experimentally-based versions of the solidus (phlogopite-free) containing less than about 0.4 wt. % H_2O, insufficient to produce the maximum amphibole. The heavy lines show where vapor-absent amphibole-peridotite begins to melt, probably by an incongruent reaction.

Peridotite-CO_2

Fig. 2, showing the effect of 0.1 wt. % CO_2 on peridotite, is valid for a wide range of CO_2 contents. The CO_2 exists as vapor at pressures below the carbonation reaction TQ, and as dolomite above this curve. More than 10 wt. % CO_2 would be required to convert all of the clinopyroxene into dolomite, leaving excess vapor at pressures above TQ for other carbonation reactions. Calcic dolomite and peridotite melt together along QR, producing low-SiO_2 carbonatitic liquids. Dolomite is replaced by magnesite at higher pressures.

Peridotite-H_2O-CO_2

Fig. 3 shows that with excess CO_2 and H_2O, the reaction TQ becomes a divariant carbonation surface, with geometry shown by contours for constant CO_2/H_2O in the vapor phase. Similarly, the solidus is a divariant surface connecting the solidus curves for excess H_2O, PM, and for excess CO_2, PQU (QU differs from QR in Fig. 2). The solidus surface for carbonated peridotite, QNU, meets the subsolidus carbonation surface along the univariant line QN. The vapor phase contours for the solidus surface
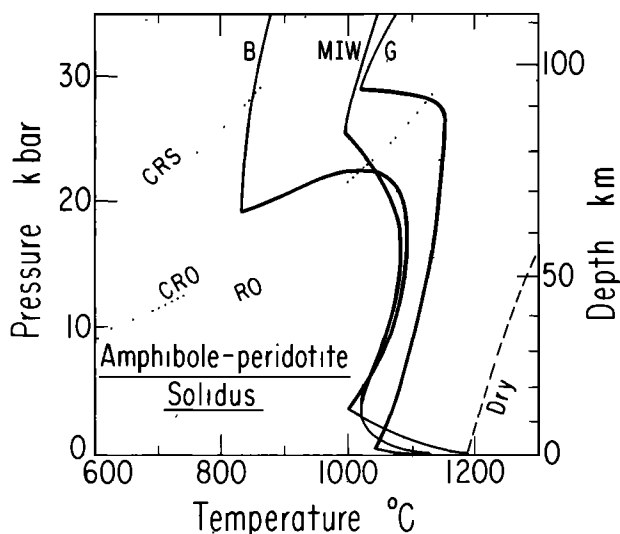

Fig. 1. Experimentally based and deduced curves for the solidus of amphibole-peridotite, with < 0.4 wt. % H_2O. Depths and geotherms are for the earth (CR = *Clark and Ringwood*, 1964; R = *Ringwood*, 1966); MIW = *Millhollen, Irving and Wyllie* (1974); B = *Boettcher* (*Mysen and Boettcher*, 1975); G = *Green* (1973); S = shield; O = oceanic.
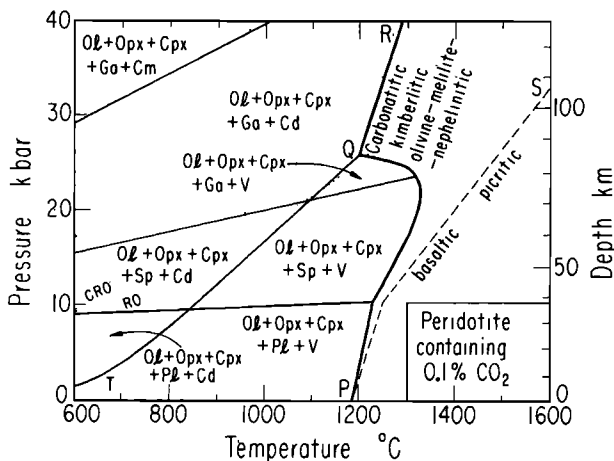
Fig. 2. Peridotite-CO_2, in part schematic. See *Eggler* (1976, 1978) and *Wyllie* (1977, 1978) for data sources. Depths and geotherms are for the earth. PS is solidus for the volatile-free peridotite. Abbreviations: Ol = olivine, Opx = orthopyroxene, Ga = garnet, Sp = spinel, Pl = plagioclase, Cd = dolomite solid solution, Cm = magnesite solid solution, V = vapor.

of uncarbonated peridotite, PQNM, illustrate a simple geometry below 20 kbar (*Mysen and Boettcher*, 1975), but in the region of the intersection line, QN, the contours on the surface pass through a temperature maximum on the line mn, before dropping down to QN. Unless there is enough CO_2 present to carbonate all of the clinopyroxene, conditions in the area QNU for melting of carbonated peridotites are not reached. Partially carbonated peridotite begins to melt along the line QN, with the vapor phase composition buffered to high values of H_2O/CO_2, as shown by the contours. In order to illustrate the effect of carbonation, the reactions for hydration to amphibole and phlogopite have been neglected in Figs. 3 and 4.

The shapes of the contours are more easily visualized in Fig. 4. Fig. 4 shows the phase fields in the presence of excess vapor of fixed composition, $X_{CO_2}^v$ = 0.6. The solidus curve is the corresponding solidus contour from Fig. 3. The reaction (6) is the carbonation reaction from Fig. 3.
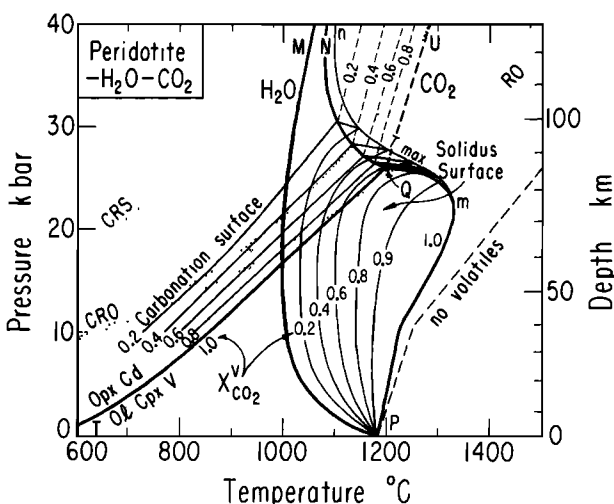

Fig. 3. Peridotite-H_2O-CO_2 with excess vapor, omitting amphibole and phlogopite, pieced together and averaged from various data sources (see *Wyllie*, 1977, 1978; *Eggler et al.*, 1976). The divariant carbonation surface divides the solidus surface into (1) the area PQNM passing through a temperature maximum along mn, for the melting of peridotite-vapor, and (2) the area QNU for the melting of carbonated peridotite-vapor. Two other carbonation reactions (not shown) intersect the latter area (see Fig. 4A). The temperature maximum mn is consistent with phase relationships deduced in the system MgO-SiO_2-CO_2-H_2O (*Ellis and Wyllie*, 1978), but its magnitude is not known (except for PmQ, pure CO_2). Depths and geotherms are for the earth.
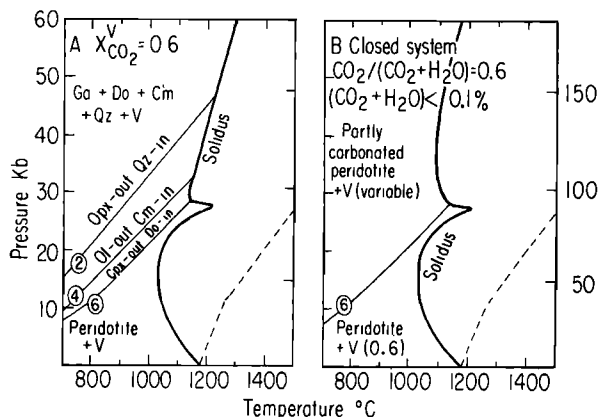

Fig. 4. Peridotite-H_2O-CO_2 with excess vapor, omitting amphibole and phlogopite. Largely schematic. The magnitude of the temperature-maximum on the solidus is not known. A. Open system, with vapor phase composition maintained constant through three carbonation reactions: (6) is TQ in Fig. 3; for details of (4) and (2) see *Wyllie and Huang* (1976) and *Wyllie* (1977). Each line is a contour for fixed vapor-phase composition, three of which are reproduced from Fig. 3. B. Closed system, reactions are identical with those in Fig. 4A at pressures below the contour for reaction (6). With increasing pressure above contour (6) carbonation proceeds and vapor is enriched in H_2O/CO_2; the solidus is part of the buffer line QN in Fig. 3. Additional abbreviation: Qz = silica polymorph.

The reactions labelled (4) and (2) are the additional carbonation reactions that occur if there is enough CO_2 present to complete the successive steps and produce a carbonate-silica assemblage, with accessory garnet.

In a closed system with a small proportion of total volatiles, and with the same vapor phase composition at low pressures, the carbonation reaction begins along the same line as in Fig. 4A. With continued reaction of
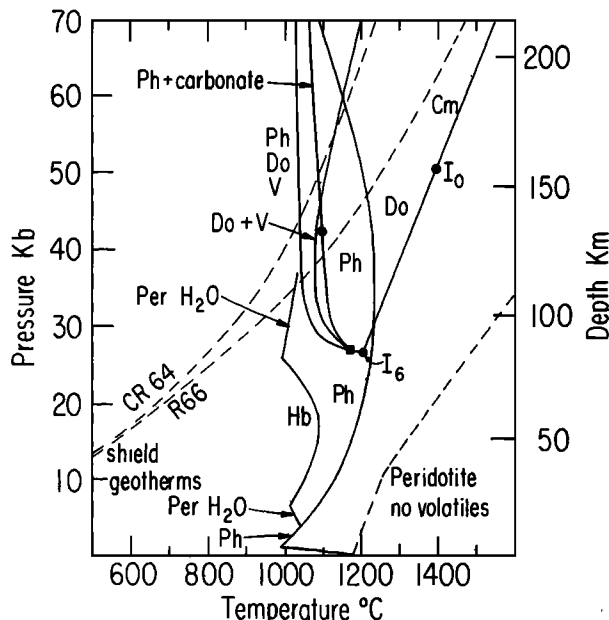

Fig. 5. Selected melting reactions for peridotite-H_2O-CO_2, partly schematic. I_6 corresponds to Q in Figs. 2 and 3. Abbreviations, see Fig. 2; additional: Ph = phlogopite, Do = dolomite solid solution (Cd in Fig. 2), Per = peridotite, volatile-free. Vapor-absent curves are shown for peridotite with Hb (Fig. 1), Ph (estimated), carbonate (Fig. 2), and Ph-carbonate. Buffered vapor-present curves are shown for peridotite with Do, and Do-Ph. Buffered vapor-present curves for peridotite with Hb or Ph are, respectively, coincident with curve Hb, and somewhat lower than curve Ph up to the invariant point near I_6 (at higher pressures Ph is jointed by Do). Depths and shield geotherms are for the earth.

CO_2 the vapor phase composition tracks across the divariant surface becoming progressively enriched in H_2O/CO_2. The solidus is divided into two parts, the low pressure part being identical with that in Fig. 4A, but the high pressure part corresponding to the vapor-phase buffer line, QN in Fig. 3. The vapor-phase at the solidus becomes progressively enriched in H_2O/CO_2 with increasing pressure along QN.

Each carbonation reaction (Fig. 4A) is represented in peridotite-H_2O-CO_2 by a divariant carbonation surface which intersects the solidus surface in a univariant line, similar to QN in Fig. 3. Similarly, each hydration reaction, involving the formation of amphibole or phlogopite, is represented in peridotite-CO_2-H_2O by a subsolidus divariant surface which intersects the solidus surface in a univariant line where the vapor phase composition is buffered, unless there is more H_2O present than that required to hydrate the peridotite completely: about 0.4 wt. % for amphibole, and 0.02 wt. % for phlogopite. The buffering capacity of the hydrous minerals is obviously much less than that of carbonates.

The estimated positions of curves for the beginning of melting of several mineral assemblages in the system peridotite-H_2O-CO_2 are compared in Fig. 5. The buffered solidus curve for Do+V extending from I_6 is the line QN from Fig. 3. A subsolidus reaction involving dolomite and phlogopite produces an invariant point near I_6 which terminates this buffer curve, and from this point there extend two additional solidus curves: one for the vapor-absent eutectic of phlogopite-carbonate-peridotite (Holloway and Eggler, 1976), and the other for the same eutectic with excess vapor, buffered to high H_2O/CO_2 because of the strong buffering capacity of dolomite. Fig. 1 shows alternative positions for the curve Hb, one of which (G) might just overlap with the Do+V curve, generating a melting reaction for Hb-Do-peridotite with buffered vapor, in a very limited region.

Applications

Figs. 1, 2, and 5 show that even trace amounts of H_2O, CO_2 or mixtures of H_2O-CO_2, whether present as vapor or stored in minerals, lower the temperature of beginning of melting of mantle peridotites through hundreds of degrees compared with the solidus for volatile-free peridotite.

For the peridotite-vapor part of the solidus surface, the SiO_2 content of the liquid is increased with H_2O/CO_2 in the vapor. There is a boundary on the surface separating quartz-normative liquids from forsterite-normative liquids (Mysen and Boettcher, 1975; Eggler, 1975). On the H_2O side of mn (Fig. 3), and at all pressures below 26 kbar, H_2O/CO_2 is greater in liquid than in vapor. On the CO_2 side of mn, above 26 kbar, CO_2/H_2O is greater in liquid than in vapor; this applies to all buffered reactions with carbonate. At high pressures, even low CO_2/H_2O in the vapor is sufficient to produce carbonate, and the presence of carbonate ensures generation of SiO_2-poor, CO_2-rich liquids. At pressures greater than 30 kbar, the vapor phase, if present, is buffered to very high H_2O/CO_2 (Fig. 3) in melting of dolomite-peridotite or phlogopite-dolomite-peridotite. The presence of phlogopite would ensure high K_2O and probably increase MgO/CaO in the small amount of liquid produced. The near-solidus liquid is probably carbonatitic for the first assemblage, and melilitic or kimberlitic for the second assemblage (Brey and Green, 1976).

For a large temperature-depth interval during the thermal evolution of a planet, melting must occur wherever H_2O and CO_2 are present. The small proportion of very fluid, low-viscosity magma must migrate, flushing out incompatible elements, and becoming concentrated as magma pockets or aborted intrusions at shallower, cooler levels. This process would produce inhomogeneities in trace element contents of mantle peridotites before temperatures became high enough for the generation of large proportions of basaltic magma.

The existence of a temperature-maximum on the solidus surface (Fig. 3) shows that a magma rising along an adiabat, not too high in temperature above the solidus (Fig. 4) would evolve its dissolved H_2O and CO_2 when it reached a depth corresponding to a pressure of about 25 kbar, if equilibrium were maintained. This could enhance the prospects of crack propagation and explosive eruption, if tectonic conditions were suitable (O.L. Anderson, personal comm., 1977).

Consider now the calculated positions of geotherms in the Earth. Figs. 1 and 5 show that the seismic low-velocity zone in oceanic regions (80-100 km) is compatible with incipient melting associated with the instability of amphibole. The lower oceanic lithosphere must become enriched in rocks similar to kaersutite eclogite. Beneath continental

shields, incipient melting must begin in the depth interval 110-170 km if the mantle peridotite contains any H_2O+CO_2 (Fig. 5). The seismic low-velocity zone beneath shields is weakly developed or absent, indicating that mantle peridotite in these regions contains little or no phlogopite, carbonate, or H_2O-CO_2 vapor. Kimberlites and other volatile-rich alkalic magmas have been erupted, however, demonstrating that H_2O and CO_2 have existed, at least locally at depth. I conclude that H_2O and CO_2 are distributed sparsely and irregularly in subcontinental mantle, with periodic magmatic flushes transporting these components into the overlying lithosphere, or through it if tectonic conditions are suitable.

Repeated magmatic activity indicates that H_2O and CO_2 must be replenished, either from deeper sources or by recycling via subducted oceanic crust. The oxygen fugacity may control the relationships among graphite or diamond, carbonate, and near-solidus carbonatitic, kimberlitic, or nephilinitic melts at various levels in the mantle.

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