THE EFFECT OF H₂O AND CO₂ ON PLANETARY MANTLES
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Abstract. The solidus for peridotite-H₂O-CO₂ 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 H₂O-CO₂ 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 CO₂ side of the maximum, above 26 kb, CO₂/H₂O is greater in liquid than in vapor, and liquids are SiO₂-poor; on the H₂O side of this maximum (including all pressures below 26 kb), H₂O/CO₂ is greater in liquid than in vapor, and liquids change from forsterite-normative to quartz-normative with increasing H₂O/CO₂ in vapor. Even traces of H₂O and CO₂, 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 H₂O and CO₂ 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-H₂O-CO₂. 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-H₂O-CO₂ 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 H₂O and CO₂ is certainly not true for all mantles at all depths at all times.

H₂O and CO₂ 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 H₂O-CO₂ fluid may reach tens of weight per cent. Amphibole, phlogopite, and carbonate can be crystalline hosts for H₂O and CO₂ at mantle pressures. Other possibilities, such as titanoclinohumite, dense hydrated magnesian silicates, and sanidine hydrate are neglected in this treatment. At temperatures above 1000°C, many peridotites can be completely hydrated by about 0.4 wt. % H₂O, with formation of amphibole. At pressures above about 30 kbar, where amphibole is not stable, it requires only about 0.02 wt. % H₂O to produce maximum phlogopite in peridotite corresponding to the earth's mantle. In contrast, about 30 wt. % CO₂ 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 H₂O in silicate liquids increases to about 10 wt. % at 5 kbar and about 20 wt. % at 20 kbar. In contrast, the solubility of CO₂ 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 CO₂ 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 H₂O and CO₂, 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 CO₂ and H₂O, and the way they are distributed among vapor, carbonates, and hydrous minerals. Common basaltic liquids are developed at higher temperatures, nearer to the solidus for volatile-free peridotite, where H₂O and CO₂ are normally so diluted in the melt that they have little effect.

Peridotite-H₂O

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. % H₂O, insufficient to produce the maximum amphibole. The heavy lines show where vapor-absent amphibole-peridotite begins to melt, probably by an incongruent reaction.

Peridotite-CO₂

Fig. 2, showing the effect of 0.1 wt. % CO₂ on peridotite, is valid for a wide range of CO₂ contents. The CO₂ exists as vapor at pressures below the carbonation reaction TQ, and as dolomite above this curve. More than 10 wt. % CO₂ 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-SiO₂ carbonatitic liquids. Dolomite is replaced by magnetite at higher pressures.

Peridotite-H₂O-CO₂

Fig. 3 shows that with excess CO₂ and H₂O, the reaction TQ becomes a divariant carbonation surface, with geometry shown by contours for constant CO₂/H₂O in the vapor phase. Similarly, the solidus is a divariant surface connecting the solidus curves for excess H₂O, PM, and for excess CO₂, PQU (QU differs from QR in Fig. 2). The solidus surface for carbonated peridotite, QNU, meets the subsolidus carbonation surface along the invariant line QN. The vapor phase contours for the solidus surface...
of uncarbonated peridotite, PQNM, illustrate a simple geometry below in Figs. 3 and 4. In a 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$_2$O/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 reactions begin to melt along the line QN, with the contour on the surface passes 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$_2$O/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 by the contours. In order to illustrate the effect of carbonation, the reaction (6) is the carbonation reaction from Fig. 3. 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 reactions begin to melt along the line QN, with the contour on the surface passes 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$_2$O/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 by the contours. In order to illustrate the effect of carbonation, the reaction (6) is the carbonation reaction from Fig. 3.
CO2 the vapor phase composition tracks across the divariant surface becoming progressively enriched in H2O/CO2. 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 H2O/CO2 with increasing pressure along QN.

Each carbonation reaction (Fig. 4A) is represented in peridotite-H2O-CO2 by a divariant 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-CO2-H2O 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 H2O 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-H2O-CO2 are compared in Fig. 5. The buffered solidus curve for DoV extending from Ia is the line QN from Fig. 3. A subsolidus reaction involving dolomite and phlogopite produces an invariant point near Ia 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 (Holliday and Eggler, 1976), and the other for the same eutectic with excess vapor. As the pressure starts to high H2O/CO2 because of the strong buffering capacity of dolomite. Fig. 1 shows alternative positions for the curve Hb, one of which (Q) might just overlap with the DoV 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 H2O, CO2 or mixtures of H2O-CO2, 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 the peridotite-vapor part of the solidus surface, the SI02 content of the liquid is increased with H2O/CO2 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 H2O side of mn (Fig. 3), and at all pressures below 26 kbar, H2O/CO2 is greater in liquid than in vapor. On the CO2 side of mn, above 26 kbar, CO2/Do is greater in liquid than in vapor; this applies to all buffered reactions with carbonate. At high pressures, even low CO2/Do in the vapor is sufficient to produce carbonate, and the presence of carbonate ensures generation of SI02-poor, CO2-rich liquids. At pressures greater than 30 kbar, the vapor phase, if present, is buffered to very high H2O/CO2 (Fig. 3) in melting of dolomite-peridotite or phlogopite-dolomite-peridotite. The presence of phlogopite would ensure high K2O and probably increase MgO/SiO2 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 H2O and CO2 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 elements of mantle peridotites before temperatures became high enough for the generation of large proportions of basaltic magmas.

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 H2O and CO2 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 (L.E. 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 H2O+CO2 (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 H2O-CO2 vapor. Kimberlites and other volatile-rich alkaline magmas have been erupted, however, demonstrating that H2O and CO2 have existed, at least locally at depth. I conclude that H2O and CO2 are distributed sparsely and irregularly in subcontinental mantle, with periodic magmatic fluxes transporting these components into the overlying lithosphere, or through it if tectonic conditions are suitable.

Repeated magmatic activity indicates that H2O and CO2 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 nephelinitic melts at various levels in the mantle.

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