Partial melt compositions of carbonated peridotite at 3 GPa and role of CO_2 in alkali-basalt magma generation

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Abstract. Partial melt compositions of natural carbonated peridotite (KLB-1 + 2.5 wt% CO_2) have been determined at 3 GPa using the diamond aggregate method. Melt obtained at 1350 °C is carbonatitic, and with increasing temperature melt composition becomes silicate-rich. These melts are lower in SiO_2 and Al_2O_3 and higher in MgO and CaO compared to dry partial melts of KLB-1 generated at the same pressure. The 1400 and 1450 °C liquids have melilititic compositions, which are in good agreement with those of natural alkali-basalts from continental regions. At higher temperatures, partial melts are richer in SiO_2, and the compositions of liquids at 1475 and 1525 °C approximate nephelinite and basanite respectively. However, they deviate from natural alkaline rocks in that the CaO/(CaO+MgO) ratios are smaller, suggesting that the natural nephelinite and basanite magmas were formed at lower pressures. The compositional trend of natural alkaline rocks, melilitites-nephelinites-basanites, may reflect the effect of decreasing pressure.

Introduction

Carbon dioxide is one of the major volatile components in the earth. Numerous melting experiments in both simple and natural carbonated peridotite systems have shown that it has a significant effect on mantle melting processes. The presence of CO_2 lowers the solidus temperature of mantle peridotite significantly at pressures where carbonate is a solidus phase and forms carbonatitic melts at the solidus rather than silicate melts. With progressive melting at higher temperatures, partial melts change to silicate melts, but they are characteristically silica-poor, suggesting that extremely silica-undersaturated alkali-basalts and kimberlites were formed in the presence of CO_2 [e.g., *Wyllie and Huang*, 1976; *Brey and Green*, 1977; *Eggler*, 1978; *Wendlandt and Mysen*, 1980; *Wallace and Green*, 1988; *Falloon and Green*, 1989].

The experimental problem that melt composition is modified at quenching by the overgrowth of adjacent minerals has prevented the precise determination of melt composition formed by the direct partial melting of peridotite. *Mysen and Boettcher* [1975] obtained silica-poor partial melts in the system peridotite-H_2O-CO_2; however, their results may have

been influenced by such quenching problem. The quantitative effect of CO_2 on partial melt composition in the natural peridotite system, therefore, is still poorly understood.

The partial melting of carbonated lherzolite was experimentally investigated at 3 GPa in this study. The compositions of partial melts were obtained using the "diamond aggregate method" which has recently been developed to determine the precise compositions of low-degree partial melts of less than 5 wt% [e.g., *Hirose and Kushiro*, 1993; *Baker and Stolper*, 1994; *Kushiro*, 1996]. Compared with the results of anhydrous melting experiments, the effect of CO_2 on partial melt compositions is examined, and its role in the generation of alkali-basalt magmas is discussed.

Experimental procedure

Natural lherzolite KLB-1 plus 5 wt% magnesite (~2.5 wt% CO_2) was used as the starting material in this study. KLB-1 has a fertile mantle composition, and its partial melt compositions have already been determined in a wide pressure range for anhydrous conditions. The KLB-1 and magnesite were mixed and ground under acetone to a grain size of 5-30 μm, and then loaded into graphite capsules with two small chips of diamond aggregate. The samples were dried in 110 °C oven before sealing in Pt outer capsules. Some amounts of CO may have been generated by the reaction of diamond/graphite with the sample. The fraction of CO in the C-O fluid, however, is less than 10 mol% at 3 GPa [e.g. *Pawley et al.*, 1992], and it does not significantly affect the solubility of CO_2 in partial melts. All experiments were performed in a 1/2-inch piston-cylinder apparatus, talc-Pyrex outer sleeves and graphite furnaces. Temperature was monitored by $W_5Re/W_{26}Re$ thermocouples. Details of the experimental conditions are summarized in Table 1. The uncertainty of pressure was less than 0.1 GPa, and the temperature gradient in the sample was approximately 10-20 °C. Partial melts migrated into the pore space of the diamond grains (40-60 μm), and they were separated from peridotite sufficiently to prevent quench modification of their compositions by the overgrowth of adjacent minerals. The major element compositions of the trapped melt patches were analyzed by using a JEOL scanning microprobe with the Link energy dispersive analyzer system (Link ISIS). Analytical conditions were 15 kV accelerating voltage, 1 nA specimen current, and 60 s counting time.

The present run duration ranged from 6 to 12 h. The result of time series experiments under dry condition with the diamond aggregate method have shown that the compositions of partial melts change little after 6 h at 1350 °C [*Hirose and Kushiro*, 1993]. Also, because the reaction rate is high in the carbonate-bearing systems, the present experimental duration is long enough for close equilibration.

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Table 1. Compositions of Partial Melts and Residual Solids

	53				54	55	56			
Run #	53				54	55	56			
P (GPa)	3				3	3	3			
T (°C)	1400				1450	1475	1525			
Time(h)	8.0				8.6	6.0	6.0			
Phases	liq	ol	opx	gar	liq	liq	liq	ol	opx	gar(tr)
SiO_2	35.99 (1.77)	42.45	55.19	43.05	38.39 (2.59)	40.23 (0.94)	42.78 (2.26)	40.95	55.36	41.99
TiO_2	0.74 (0.10)	n.d.	0.03	0.25	1.11 (0.20)	0.61 (0.12)	0.60 (0.06)	0.10	0.05	0.29
Al_2O_3	8.84 (1.26)	0.16	4.32	22.31	8.28 (1.06)	10.95 (1.21)	10.59 (1.69)	0.08	5.01	21.39
FeO^*	10.40 (0.85)	8.24	5.70	4.94	9.24 (1.13)	10.49 (1.55)	10.43 (0.72)	7.53	4.44	6.75
MnO	0.05 (0.09)	0.38	0.04	0.43	0.06 (0.14)	0.01 (0.55)	0.06 (0.19)	0.30	0.35	0.38
MgO	22.94 (1.30)	49.52	32.63	21.81	24.30 (1.81)	23.08 (1.07)	24.87 (0.55)	49.21	32.53	21.07
CaO	18.54 (1.98)	0.21	1.27	5.25	16.67 (1.65)	12.39 (0.82)	9.34 (0.56)	0.25	1.43	5.95
Na_2O	2.23 (0.52)	n.d.	n.d.	n.d.	1.55 (0.37)	1.87 (0.36)	1.16 (0.09)	n.d.	n.d.	n.d.
K_2O	0.09 (0.08)	n.d.	n.d.	n.d.	0.10 (0.11)	0.05 (0.07)	0.01 (0.03)	n.d.	n.d.	n.d.
Cr_2O_3	0.19 (0.08)	0.18	0.71	2.59	0.29 (0.13)	0.31 (0.15)	0.17 (0.10)	0.19	0.80	1.74
Fo	91.1-91.5				91.3-92.2	91.3-92.3	91.6-92.2			
†Kd	0.365				0.396	0.327	0.364			

Numbers in parentheses are one standard deviation of averages. Total Fe as FeO^*. $^\dagger Kd(Fe^*/Mg)$. Phases are liq, liquid; ol,olivine; opx, orthopyroxene; gar, garnet; tr, trace phase.

Results and discussion

Partial melt composition of carbonated peridotite

The compositions of partial melts of carbonated KLB-1 were obtained in the temperature range 1350-1525 °C (Table 1). The dry KLB-1 solidus temperature is just below 1500 °C at this pressure [Hirose and Kushiro, 1993]. In all experiments, liquid coexisted with olivine, orthopyroxene, and garnet, without any carbonate minerals. The selected analyses of rim

of solid phases found in run at 1400 and 1525 °C are presented in Table 1.

Melt obtained at 1350 °C is a carbonate-rich melt containing some silicate [Wallace and Green, 1988; Thibault et al., 1992; Dalton and Wood, 1993; Sweeney, 1994]. The melt pockets trapped between the diamond grains were most likely too small (less than 10 μm) to have average composition of carbonatitic melt, because it was quenched to an aggregate of quench crystals [e.g., Wallace and Green,
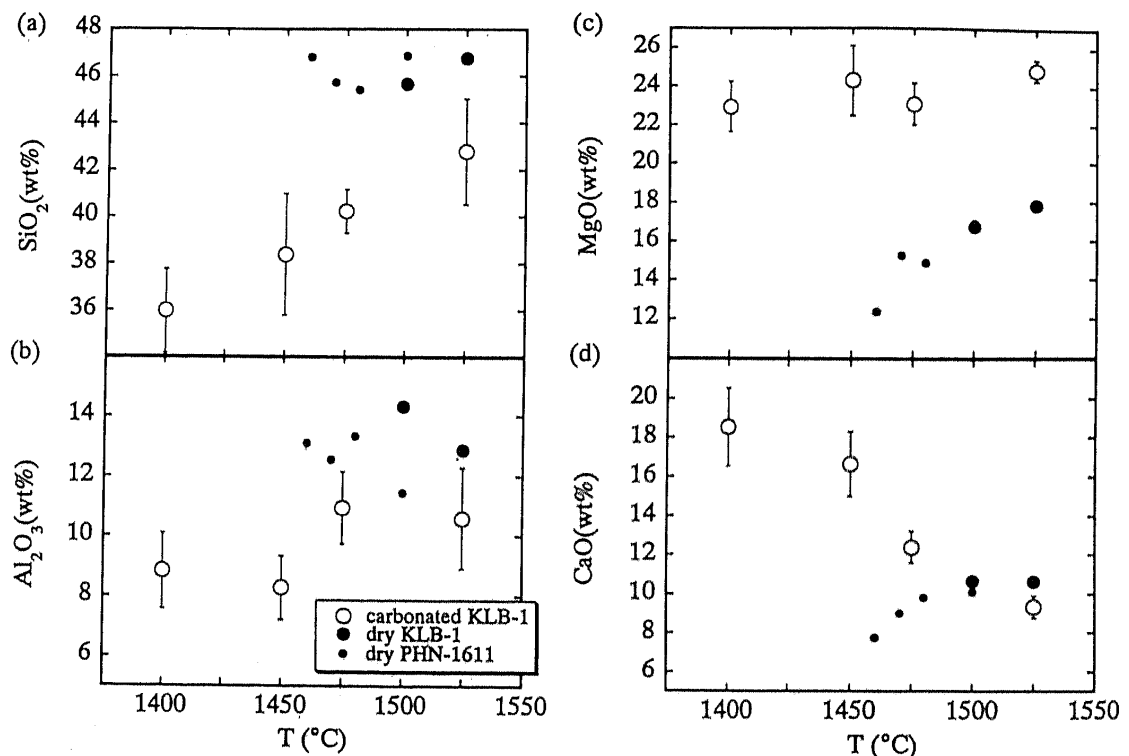

Figure 1. Compositional variation of melts formed by partial melting of carbonated and dry peridotites at 3 GPa. The compositions of dry partial melts were also determined by the diamond aggregate method [Hirose and Kushiro, 1993; Kushiro, 1996]. Error bars indicate 1σ.

1988; *Lee and Wyllie*, 1997]. Although the analysis might not represent the precise liquid composition, it shows that the melt contains ~3 wt% SiO_2, ~1 wt% Al_2O_3, ~14 wt% MgO, and ~25 wt% CaO. *Wallace and Green* [1988] and *Sweeney* [1994] suggested that in peridotite-CO_2-H_2O systems, the stability of carbonatite melt is restricted to less than 1200 °C at 3 GPa. The present result shows that carbonatitic melt is formed (silicate melt is not formed) from peridotite even at 1350 °C in the H_2O-free system, which is consistent with the results of *Dalton and Wood* [1993].

Above 1400 °C, silicate-rich melts were formed. They were quenched to a glass that was relatively inhomogeneous from melt pocket to pocket when compared to those in the previous diamond aggregate experiments under dry conditions [e.g., *Hirose and Kushiro*, 1993; *Baker and Stolper*, 1994]. The partial melt has 36 wt% SiO_2 at 1400 °C, and also contains much higher abundances of Al, Fe, Mg and Na but less Ca content than the carbonatite melt. They are melilititic in composition at 1400 and 1450 °C, and with increasing temperature they become nephelinitic at 1475 °C and basanitic at 1525 °C [*Le Bas*, 1989]. The compositional change of partial melts as a function of temperature is shown in Figure 1. The SiO_2 content of partial melts monotonically increases with temperature to 43 wt% at 1525 °C. The Al_2O_3 content of the silicate-rich partial melts remains approximately constant at 8-10 wt%. Similar results have been obtained in melting experiments on dry peridotite at 3 GPa where the Al_2O_3 content changed little providing garnet was present in the residue [*Kushiro*, 1996]. The FeO* (total Fe as FeO) content is almost constant, and the MgO content increases slightly with temperature. The CaO content of the partial melts, all of which were obtained in the absence of residual clinopyroxene, dramatically decreases with increasing temperature from 19 wt% at 1400 °C to 9 wt% at 1525 °C. These results confirm the conclusions of *Wyllie and Huang* [1976], *Eggler* [1978], and *Adam* [1988] in the model systems CaO-MgO-Al_2O_3-SiO_2-CO_2.

The addition of CO_2 expands the stability fields of garnet and orthopyroxene as shown previously [e.g. *Brey and Green*, 1977; *Adam*, 1988]. The crystalline phase assemblage of carbonated KLB-1 is olivine+orthopyroxene+garnet in the temperature range 1350-1525 °C, whereas that of dry KLB-1 is olivine+orthopyroxene+clinopyroxene at 1500-1525 °C [*Hirose and Kushiro*, 1993]. The disappearance of clinopyroxene suggests that it reacted in the reaction magnesite+clinopyroxene→dolomite+orthopyroxene [*Brey et al.*, 1983] and melted out at low degree of partial melting [*Dalton and Wood*, 1993].

The effect of CO_2 on partial melt composition can be compared to the results of dry peridotite melting experiments at the same pressure. Partial melt compositions of dry lherzolites KLB-1 and PHN-1611 [*Hirose and Kushiro*, 1993; *Kushiro*, 1996] and of carbonated KLB-1 are shown in Figure 1. The PHN-1611 has slightly lower Al and higher Fe contents than KLB-1, which accounts for the slight differences between their partial melts in Al_2O_3 and FeO* contents. The carbonated peridotite used in this study was a mixture of KLB-1 and magnesite, which leads to an enrichment in MgO in KLB-1. The most significant effect of this enrichment is probably a depletion of iron in the partial melts [*Hirose and Kushiro*, 1993; *Baker and Stolper*, 1994]. The present experiments show that the compositions of silicate-rich melts formed from carbonated peridotite are characterized by low SiO_2 and Al_2O_3

and high MgO and CaO contents compared to those of dry partial melts. With increasing temperature, the SiO_2 and CaO contents change considerably and the partial melt composition of carbonated peridotite approaches that of dry melt formed at the equivalent temperature; however, they are still deficient in SiO_2 and enriched in MgO compared to dry partial melt even at 1525 °C.

Generation of alkali-basalt magmas

The present experiments show that a wide range of partial melt compositions are obtained by changing temperature conditions. The compositions of natural alkali-basalts from continental and oceanic regions are plotted in Figure 2. To minimize the effect of crystal fractionation, only primitive compositions (0.5-1.0 FeO*/MgO) are presented. The continental alkali-basalts define trends in both the SiO_2-Al_2O_3 and SiO_2-CaO diagrams, showing that Al_2O_3 decreases

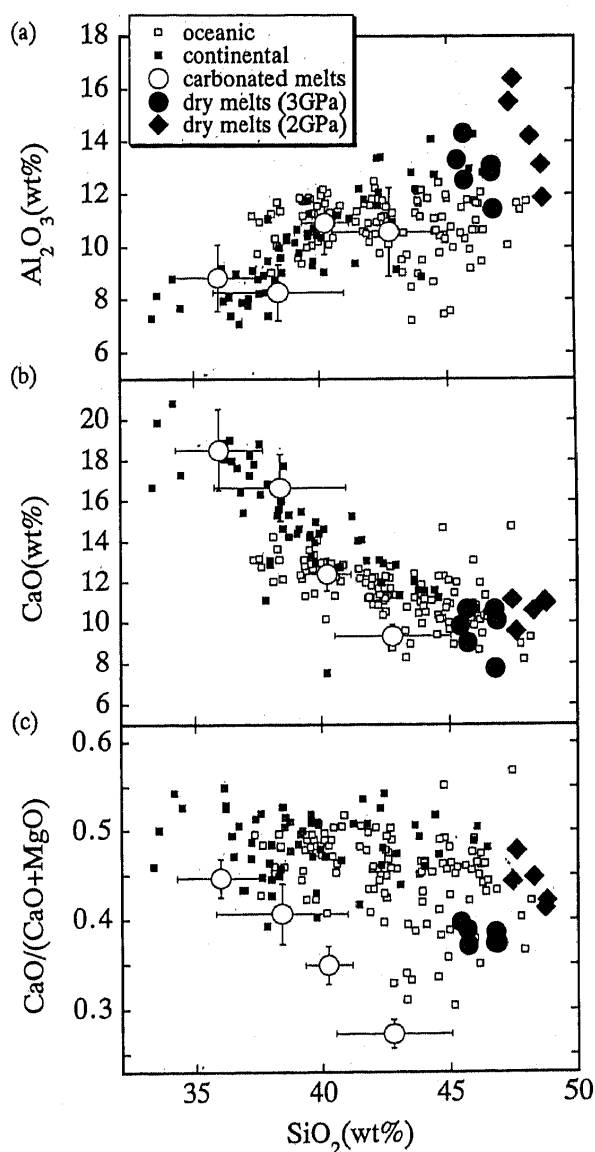**Figure 2.** Compositional variation of primitive alkali basalts from oceanic and continental regions (FeO*/MgO <1) [*Alibert et al.*, 1983; *Brey*, 1978; *Hegner et al.*, 1995; *Wedepohl et al.*, 1994; *Wilson and Downes*, 1991; *Wilson et al.*, 1995; *Cheng et al.*, 1993; *Clague and Frey*, 1982; *Dupuy et al.*, 1989; *Hoernle and Schmincke*, 1993; *Maaløe et al.*, 1992].

and CaO increases with decreasing SiO_2 [Brey, 1978; Adam, 1988]. Those from oceanic islands have also higher CaO contents with decreasing SiO_2 but have roughly constant 9-12 wt% Al_2O_3. Compositions of the 1400 and 1450 °C liquids are in good agreement with those of natural melilitites from continents. This confirms that CO_2 is responsible for the compositions of such silica-undersaturated magmas found in continental rift and cratonic regions. The 1475 and 1525 °C liquids are also similar to natural nephelinites or basanites in SiO_2, Al_2O_3 and CaO contents. However, they deviate from the alkali-basalt field in CaO/(CaO+MgO) ratios, although some of the oceanic alkali-basalts have close values. This strongly suggests that natural nephelinitic and basanitic magmas may not be formed by high temperature melting at 3 GPa but alternatively that they could be produced at lower pressures in the presence of CO_2. CO_2 has a much smaller effect on the partial melt composition at lower pressures, because the solubility of CO_2 in the melt is much lower. The lower pressure partial melts of carbonated peridotite, therefore, may have natural nephelinite or basanite compositions with a higher content of SiO_2 and Al_2O_3, a lower content of FeO*, MgO and, CaO, and similar CaO/(CaO+MgO) ratios to melilitites formed at 3 GPa. The compositional trend of natural alkaline rocks, melilitites-nephelinites-basanites, may reflect the effect of decreasing pressure.

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