

CO<sub>2</sub> AS A VOLATILE COMPONENT OF THE MANTLE

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There appears to be wide agreement among petrologists that the volatiles CO<sub>2</sub> and H<sub>2</sub>O are important components of kimberlite. There is less agreement on the relative proportions of H<sub>2</sub>O and CO<sub>2</sub> and on the role of the volatiles -- whether they occurred primarily in a low-density vapor phase, or in immiscible carbonatite melt (Koster van Groos and Wyllie, 1973), or dissolved in silicate melt, either a melt of kimberlite affinity (Dawson, 1971) or a melt encountered by the kimberlite on its eruptive path (Boyd and Nixon, 1973). This study is a determination of phase equilibria in the system Mg<sub>2</sub>SiO<sub>4</sub>-SiO<sub>2</sub>-H<sub>2</sub>O-CO<sub>2</sub> at 20 kbar. The system is considered to be a simple model of a peridotitic mantle, as it contains two of the four principal peridotite phases, forsterite (Fo, Mg<sub>2</sub>SiO<sub>4</sub>) and enstatite (En, MgSiO<sub>3</sub>), plus two volatile components. The study provides information on three questions, the solubility of CO<sub>2</sub> in silicate melt, the role of CO<sub>2</sub> in solution of silicates in vapor, and the role of CO<sub>2</sub> in determining the composition of magmas produced by melting of peridotite.

Solubility of CO<sub>2</sub> in silicate melt. Experiments have been previously conducted on the solubility of CO<sub>2</sub> in silicate melts, at 20 kbar, with the compositions CaMgSi<sub>2</sub>O<sub>6</sub>, MgSiO<sub>3</sub>, and NaAlSi<sub>3</sub>O<sub>8</sub> (Eggler, 1973). Solubilities ranged from 9.5 wt % (34 mole %) in relatively basic CaMgSi<sub>2</sub>O<sub>6</sub> melt to only 0.9 wt % (5 mole %) in relatively acidic NaAlSi<sub>3</sub>O<sub>8</sub> melt. Melts containing H<sub>2</sub>O in addition to CO<sub>2</sub> dissolve slightly more CO<sub>2</sub>. At pressures at least to 30 kbar, a large miscibility gap exists between silicate melts and H<sub>2</sub>O-CO<sub>2</sub> vapor (see Fig. 1). For all compositions, CO<sub>2</sub> is much less soluble than H<sub>2</sub>O; the vapor-absent region is much smaller for compositions containing more CO<sub>2</sub> (see, for example, relations involving the four-phase tetrahedron Fo-En-L-V at 1450° C (Fig. 1)). Melt of MgSiO<sub>3</sub> composition dissolves a maximum of about 3.7 wt % CO<sub>2</sub> at 20 kbar. In Fig. 1 the melt region is outlined by a "caterpillar" shape and is drawn on the assumption of negligible CO<sub>2</sub> solution in SiO<sub>2</sub> melt.

Vapor composition. The kimberlite vapor phase is often assumed to dissolve excess alkalis (Boyd and Nixon, 1973; Koster van Groos and Wyllie, 1973). Experiments on this effect are uncompleted; however, the considerable effect of CO<sub>2</sub> in reducing solution of silica is shown schematically in Fig. 1 and in more detail in the subsolidus region of the system En-H<sub>2</sub>O-CO<sub>2</sub> in Fig. 2. When subsolidus vapor contains more H<sub>2</sub>O than 0.65 mole %, vapor dissolves sufficient silica in excess of stoichiometric MgSiO<sub>3</sub> that the assemblage is Fo+En+V. However, in more CO<sub>2</sub>-rich vapor, very little excess silica dissolves, producing En+V.

Melting relations. In the system Mg<sub>2</sub>SiO<sub>4</sub>-SiO<sub>2</sub>-H<sub>2</sub>O, compositions of liquids in equilibrium with Fo and En can be either silica-oversaturated or silica-undersaturated, depending on whether or not enstatite melts to a liquid in equilibrium with forsterite. Kushiro, Yoder, and Nishikawa (1968) have demonstrated these relations at a pressure of 10 kbar. Eggler (1973) confirmed this behavior at 20 kbar. At 20 kbar the assemblage Fo+En+V melts to H<sub>2</sub>O-saturated liquid at 1305° C. At temperatures below 1400° C, liquids in equilibrium with Fo+En are silica-oversaturated while at temperatures above 1400° C, they are silica-undersaturated. The effect of CO<sub>2</sub> on this relation was studied in the join 5MgSiO<sub>3</sub>:

$4\text{CO}_2\text{-H}_2\text{O}$  (Fig. 2). Two points are of interest: first, that the solidus temperature is higher in the presence of  $\text{CO}_2$ , and second, that the temperature at which  $\text{Fo}+\text{En}$  are no longer in equilibrium with silica-oversaturated liquid (that is, where  $\text{Fo}+\text{En}+\text{L}+\text{V}$  is no longer a stable assemblage on the join  $\text{En-H}_2\text{O-CO}_2$ ) is still  $1400^\circ\text{C}$ .

Phase relations are clarified in the semi-schematic Figure 1. In the system  $\text{Mg}_2\text{SiO}_4\text{-SiO}_2\text{-H}_2\text{O}$  the assemblage  $\text{Fo}+\text{En}$  is in equilibrium with

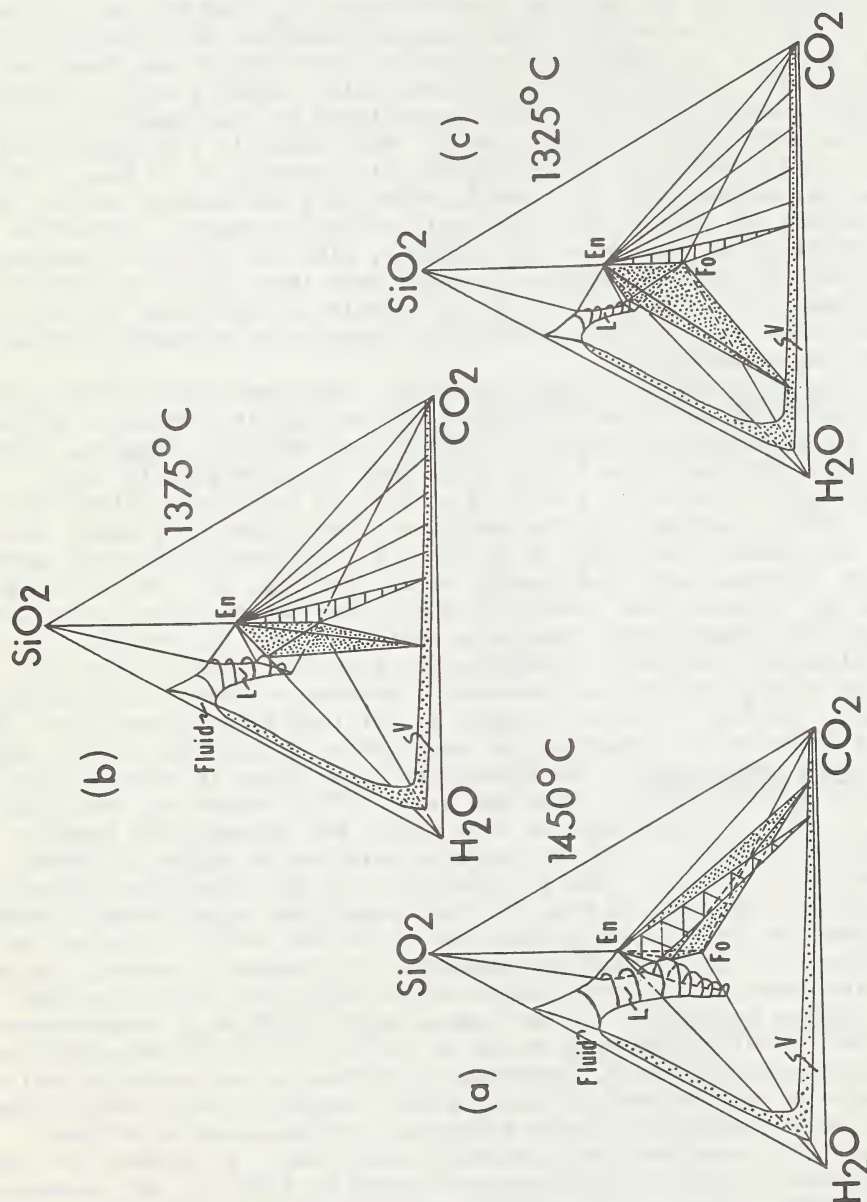


Figure 1. Phase relations (semi-schematic) in the system  $\text{Fo-En-H}_2\text{O-CO}_2$  at 20 kbar pressure (wt %). Stippled areas outline the vapor field and the four-phase tetrahedron  $\text{Fo-En-L-V}$ .

silica-oversaturated,  $\text{H}_2\text{O}$ -rich melt at temperatures below  $1400^\circ\text{C}$ , whereas above  $1400^\circ\text{C}$  those phases are in equilibrium with silica-undersaturated, less  $\text{H}_2\text{O}$ -rich melt. Figure 1 shows that in the presence of  $\text{CO}_2$  the same situation holds (the difference is that, in the presence of  $\text{CO}_2$ , the solidus of a peridotite is considerably higher in temperature than  $1305^\circ\text{C}$ ). At  $1375^\circ\text{C}$ , the stippled tetrahedron is the four-phase volume  $\text{Fo}+\text{En}+\text{L}+\text{V}$ ; the vapor contains about 45 wt %  $\text{CO}_2$  and excess  $\text{SiO}_2$ . The liquid, which is silica-oversaturated, contains about 3.5%  $\text{CO}_2$  and 10%  $\text{H}_2\text{O}$ . Back of that tetrahedron is the three-phase volume  $\text{Fo}+\text{En}+\text{L}$ ; these vapor-absent liquids are also silica-oversaturated. Compositions on the plane  $\text{En}-\text{H}_2\text{O}-\text{CO}_2$  or in the volume  $\text{Fo}-\text{En}-\text{H}_2\text{O}-\text{CO}_2$  lying to the right of the stippled tetrahedron do not melt at  $1375^\circ\text{C}$ .

At  $1400^\circ\text{C}$ ,  $\text{En}$  and  $\text{Fo}$  are in equilibrium with a slightly more  $\text{CO}_2$ -rich vapor and with a liquid that now lies exactly on the plane  $\text{En}-\text{H}_2\text{O}-\text{CO}_2$  and is exactly silica-saturated. It is clear that the presence of  $\text{CO}_2$ , even in amounts sufficient to saturate the liquid and produce a free vapor phase, does not alter the silica-saturated or undersaturated nature of the melt. At  $1450^\circ\text{C}$ ,  $\text{En}+\text{Fo}$ , both in equilibrium with a  $\text{CO}_2$ -rich vapor and in the vapor-absent region, are in equilibrium with silica-undersaturated liquids. At  $1325^\circ\text{C}$ , all liquids, even those in equilibrium with  $\text{Fo}$  or  $\text{Fo}+\text{V}$ , are silica-oversaturated.

The assemblage  $\text{Fo}+\text{En}$  is a model peridotite. Figure 1 shows that the temperature at which that assemblage melts is a function of the  $\text{H}_2\text{O}-\text{CO}_2$  content of the source region. The composition of the first-formed melt is a function of temperature (and indirectly, therefore, of  $\text{H}_2\text{O}-\text{CO}_2$  ratio). Compositions containing more than 55 mole %  $\text{CO}_2$  will melt above  $1400^\circ\text{C}$ , and liquids are silica-undersaturated. These relationships hold whether or not the liquids are vapor-saturated.

The dominance of the melting behavior of enstatite in controlling composition of melts produced from peridotite is seen from experiments of Mysen (1973). He has found a change in composition of liquids produced by melting natural peridotite from silica-oversaturated to undersaturated at nearly the same  $\text{CO}_2-\text{H}_2\text{O}$  ratio (0.55) as in the simple system discussed here.

**Conclusions.** Petrologic studies of kimberlite and related rocks have indicated that a  $\text{CO}_2-\text{H}_2\text{O}$  vapor phase was involved in their origin. This phase equilibria study indicates at least three reasons why such vapor associated with kimberlite and alkaline rocks should be  $\text{CO}_2$ -rich: (1) The model system  $\text{Fo}-\text{En}-\text{H}_2\text{O}-\text{CO}_2$  indicates that in the presence of  $\text{CO}_2$  or  $\text{CO}_2-\text{H}_2\text{O}$  mixtures peridotite comprising the upper mantle melts at higher temperature. Although the presence of  $\text{CO}_2$  has little effect on the silica-saturated or undersaturated nature of liquid produced by partial melting at any particular temperature, liquids produced at higher temperatures are less silica-saturated because of the "enstatite effect". Higher melting temperatures also produce a smaller degree of melting, at any point along the geotherm, yielding more alkalic melts. The effect of  $\text{CO}_2$  is therefore the production of less silica-saturated, more alkalic, melts. There may be primordial areas of the mantle rich in  $\text{CO}_2$ , or  $\text{CO}_2$ -rich vapor may rise to certain localities. Mantle regions with vapor richer in  $\text{H}_2\text{O}$  would melt more completely to yield silicic magmas. (2) Silicate melts dissolve rather large amounts of  $\text{H}_2\text{O}$  at high pressures. The presence of a free vapor is unlikely. Melts dissolve much less  $\text{CO}_2$ , so that the miscibility gap between melt and  $\text{CO}_2$ -rich vapor is wider, and the presence of a free vapor is more likely.



(3) Vapor rich in  $\text{CO}_2$  does not dissolve excess silica, unlike  $\text{H}_2\text{O}$ -rich vapor and may well dissolve excess alkalis. Such vapors would produce many alteration effects observed in kimberlite.

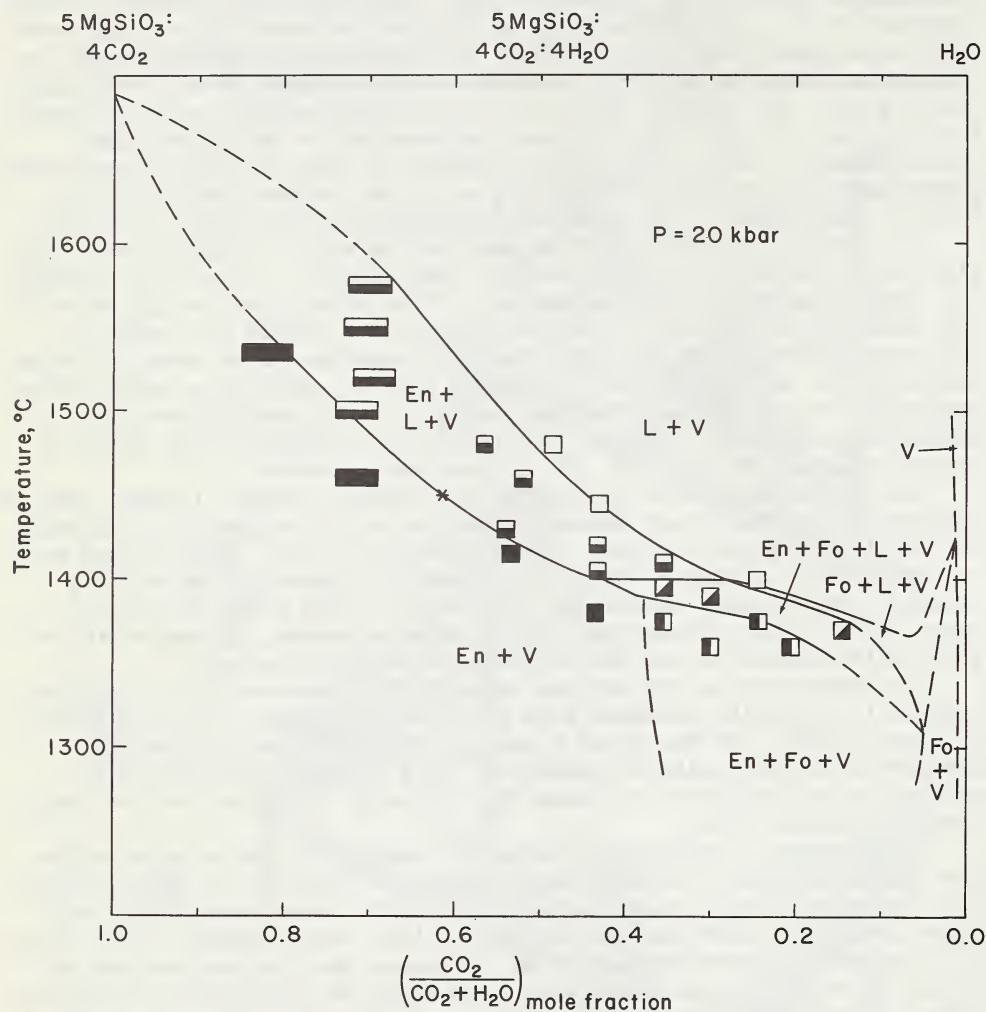


Figure 2. Phase relations on the join  $5\text{MgSiO}_3\text{:}4\text{CO}_2\text{-H}_2\text{O}$  at 20 kbar.

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