

## Melting relationships in the system $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$ at 1 kilobar pressure

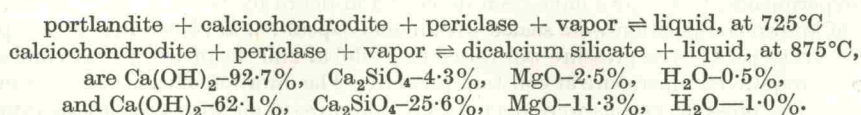
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**Abstract**—Solid-liquid-vapor phase relationships in the system  $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O}$  have been determined at 1 kilobar pressure using the quench technique in cold-seal pressure vessels. The phase fields intersected by the composition joins  $\text{Ca(OH)}_2\text{-Mg}_2\text{SiO}_4$  and  $\text{Ca(OH)}_2\text{-MgSiO}_3$  have been delineated in the temperature range 700–950°C. From these results and from previous work in the bounding systems, a schematic diagram for the phase relationships on the vapor-saturated liquidus surface has been prepared. A thermal divide exists on this surface, corresponding to the melting of mixtures on the join  $\text{Ca}_2\text{SiO}_4\text{-MgO}$  in the presence of  $\text{H}_2\text{O}$  vapor. Original liquids with compositions on the  $\text{SiO}_2$  side of the divide yield anhydrous crystalline phases and vapor on fractional crystallization, whereas original liquids with compositions on the  $\text{CaO}$  side of this divide yield hydrated crystalline phases (calciochondrodite and portlandite) plus vapor. The estimated compositions of isobaric invariant liquids at 1 kilobar pressure for the reactions:



These results provide a basis for interpretation of the phase relationships in the more complex system  $\text{CaO-MgO-SiO}_2\text{-CO}_2\text{-H}_2\text{O}$  which have bearing on the petrogenetic relationships between kimberlites and carbonatites.

### INTRODUCTION

THE field evidence that many carbonatites are intrusive and possibly magmatic was incompatible with available experimental data until WYLLIE and TUTTLE (1960) demonstrated that liquids in the system  $\text{CaO-CO}_2\text{-H}_2\text{O}$  precipitate calcite at temperatures down to 640°C through a wide pressure range. Liquids in this system were described as "synthetic carbonatite magmas". Systems more complex than  $\text{CaO-CO}_2\text{-H}_2\text{O}$  have been investigated in efforts to elucidate two problems: the physical and chemical nature of carbonatite magmas if they exist, and the origin of carbonatites. The second problem has been examined by studying the phase relationships in systems containing the "synthetic carbonatite magma" and silicate minerals occurring in rocks associated with carbonatites.

The increasing awareness in recent years of possible genetic connections between kimberlites and carbonatites (VON ECKERMANN, 1948, 1958; SAETHER, 1957; DAWSON, 1964; GARSON, 1962; DAVIDSON, 1964) led to the selection of forsterite and enstatite as suitable additional mineral components, giving sections through the five-component system  $\text{CaO-MgO-SiO}_2\text{-CO}_2\text{-H}_2\text{O}$ . It has been established in other systems such as  $\text{CaO-SiO}_2\text{-CO}_2\text{-H}_2\text{O}$  (HAAS and WYLLIE, 1963; WYLLIE and HAAS,

1965) that the phase behavior of portlandite,  $\text{Ca}(\text{OH})_2$ , can be used as a guide to the phase behavior of compositions on the join  $\text{CaCO}_3\text{--Ca}(\text{OH})_2$ . The phase relationships in the system  $\text{CaO--MgO--SiO}_2\text{--H}_2\text{O}$ , which are described in this paper, thus serve as a basis for interpretation of the phase relationships in the more complex system  $\text{CaO--MgO--SiO}_2\text{--CO}_2\text{--H}_2\text{O}$  (FRANZ, 1965), which will be described in a subsequent paper.

#### EXPERIMENTAL PROCEDURE

##### *Starting materials*

Commercial calcium hydroxide, magnesium oxide and silicic acid were used as source materials. These were prepared as described below, mixed in the desired proportions using a mechanical shaker (Wig-L-Bug Amalgamator), and stored in closed polyethylene vials within a desiccator containing  $\text{NaOH}$  and  $\text{CaSO}_4$ . *Calcium hydroxide*: A sample from a newly opened bottle of Fisher certified reagent was dried at  $240^\circ\text{C}$  for 2 hours. It was found that this gave optimum dehydration with minimum absorption of  $\text{CO}_2$ . *Magnesium oxide*: Fisher certified reagent was ignited at  $1200^\circ\text{C}$  for 1 hour. *Silica*: Matheson silicic acid ignited at  $1200^\circ\text{C}$  for 24 hours was used as a source of silica. *Forsterite*: synthetic forsterite was prepared by sintering the appropriate weight of  $\text{MgO}$  and silicic acid, and used instead of mechanical mixtures of  $\text{MgO}$  and  $\text{SiO}_2$  in order to confirm that different starting materials yielded the same products. Mixtures were prepared on the two composition joins  $\text{Ca}(\text{OH})_2\text{--Mg}_2\text{SiO}_4$  and  $\text{Ca}(\text{OH})_2\text{--MgSiO}_3$ , which will henceforth be referred to as the "forsterite join" and the "enstatite join", respectively. These joins are illustrated in Fig. 1 and 3, and the mixtures made up are shown by the runs in Fig. 4.

##### *Equipment and method*

The experimental techniques have been described in detail by WYLLIE and TUTTLE (1960). Samples of known composition were sealed within gold capsules and placed in cold-seal pressure vessels (TUTTLE, 1949). The pressure was raised to 1 kilobar and the pressure vessel and samples raised to the required temperature at constant pressure. The duration of runs varied from 1 hour to 40 days. The pressure vessels were quenched in compressed air with pressure maintained at 1 kilobar, and the temperature was reduced to below  $100^\circ\text{C}$  in 3 min. A few runs were quenched to a temperature below  $100^\circ\text{C}$  in less than 1 min by immersing the pressure vessel in cold water. No significant differences were noted between products obtained from the two quenching techniques. The samples were carefully removed from the gold capsule, and the phases present at the conditions of the run were determined from a combination of examination of the physical characteristics of the charge, petrographic observations of the crushed sample, and X-ray powder diffraction patterns. Temperature measurements were precise to  $\pm 5^\circ\text{C}$ , and the accuracy is believed to be better than  $\pm 10^\circ\text{C}$ . The precision of pressure measurements was  $\pm 20$  bars.

All reactions occurred rapidly, and there is good evidence that equilibrium was achieved. We assume that this was stable and not metastable. Runs varying in length from 1 hour to 40 days yielded consistent results. Runs on the join  $\text{Ca}(\text{OH})_2\text{--Mg}_2\text{SiO}_4$  made with different starting materials (synthetic forsterite or a mixture of  $\text{MgO}$  and  $\text{SiO}_2$ ) yielded the same results. Reversibility was established by holding a sample at a selected temperature long enough to produce the phase assemblage characteristic for that temperature, and then lowering the temperature to a level where another phase assemblage should develop, and quenching the run after an hour or two. The lower-temperature assemblage developed with no evidence remaining for the former existence of the higher-temperature assemblage. The results obtained on the basis of the method of interpretation adopted are consistent with the phase rule, and they provide a consistent phase diagram.

##### *Identification of phases*

For convenience, the phases are identified by abbreviations. The phases encountered were: portlandite (CH),  $\text{Ca}(\text{OH})_2$ ; calciochondrodite (Ch),  $\text{Ca}_6(\text{SiO}_4)_2(\text{OH})_2$ ; dicalcium silicate ( $\text{C}_2\text{S}$ ),  $\text{Ca}_2\text{SiO}_4$ ; periclase (P),  $\text{MgO}$ ; merwinite (Me),  $\text{Ca}_3\text{MgSi}_2\text{O}_8$ ; liquid (L), with composition near