

New Data on Forsterite and Monticellite Solid Solutions

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Abstract

Portions of the solvi in the system forsterite-monticellite were studied at 1440°C, 1463°C, 1481°C, and 1496°C by determining with an electron microprobe the compositions of coexisting crystals of forsterite and monticellite solid solutions which were crystallized from the "dry" melts with compositions off the system forsterite-monticellite.

The extent of the forsterite solid solution determined in this study is less than any of those reported by the previous investigators. The monticellite limb obtained with the present method appears to be more sensitive to the change in temperature than has been suggested before.

Introduction

The suggestion that CaO content in olivines could be a potential environmental indicator for the crystallization of olivines and their host rocks (Simkin and Smith, 1970) inspired the present study on the limits of forsterite (Fo_{ss}) and monticellite solid solutions (Mo_{ss}), concerning which there are serious disagreements among the investigators. The limits of solid solutions on the system forsterite-monticellite above 1400°C at atmospheric pressure reported by Ricker and Osborn (1954) differed greatly from those reported by Biggar and O'Hara (1969) (Fig. 1). The experimental and analytical methods were essentially the same in these two reports, except that Ricker and Osborn used glasses as starting material, whereas Biggar and O'Hara used gels. Using crystalline mixtures of the end members as starting material and the same experimental and analytical methods, Warner (1971) reported a limit of 27.5 ± 2.5 wt percent monticellite in forsterite solid solution and 22.5 ± 2.5 wt percent forsterite in monticellite solid solution near 1450°C. The former value was close to that of Ricker and Osborn (1954), but the latter was close to that of Biggar and O'Hara (1969).

Failure to attain equilibrium, resulting from the slow reaction rate in the solid state even at temperatures above 1400°C, appears to be responsible for these conflicting results. Metastable periclase crys-

tallizes readily from glass or gel and persists in the run product. Fo_{ss} might fail to dissolve metastable Mo_{ss} when crystallized from gel and stable Mo_{ss} might fail to nucleate when devitrified from glass (Biggar and O'Hara, 1969). Biggar and O'Hara (1969) concluded that the problems of obtaining equilibrium were not overcome in their study even with experimental times longer than those used by other investigators. In addition, the limit of detectability of X-ray diffraction and the slight changes in lattice spacings with changing compositions undoubtedly restricted the accuracy of their analyses.

Thus, it is clear that any attempts to obtain better data on the limit of Fo_{ss} or Mo_{ss} must include methods to accelerate the reactions as well as a better analytical technique to determine the compositions of the solid solutions. In the present study, coexisting Fo_{ss} and Mo_{ss} were crystallized in the presence of substantial amount of liquid between 1440°C and 1496°C at atmospheric pressure and were analyzed with an electron microprobe.

Method of Study

The chemical reaction or crystallization proceeds faster when a catalytic liquid is present than when the system is dry. Thus, the kinetic difficulties in crystallizing an equilibrium assemblage of Fo_{ss} and Mo_{ss} in a reasonably short period of time could be overcome by crystallizing them in the presence of liquid. While Fo_{ss} + Mo_{ss} + liquid equilibrium can be obtained only at the temperature of invariant point from a starting material with a bulk compo-

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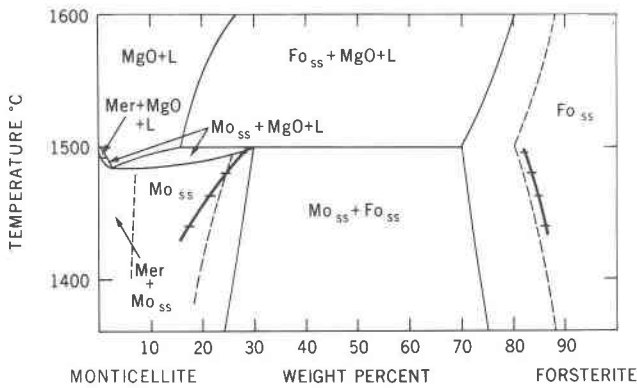


FIG. 1. Phase relations of the portion of the system forsterite-monticellite determined by Ricker and Osborn (1954) are shown in light solid lines. Solidus and solvi reported by Biggar and O'Hara (1969) are shown in dashed lines. The results of the present study are shown in heavy solid curves. Abbreviations: Fo_{ss} , forsterite solid solution; Mo_{ss} , monticellite solid solution; L, liquid; Mer, merwinite.

sition on the join Mo-Fo, the phase relations of the system CaO-MgO-SiO₂ (Ricker and Osborn, 1954) indicate that equilibrium can be obtained at any temperature between 1502°C and 1430°C from a starting material with a bulk composition removed from the join Fo-Mo.

Glasses with bulk compositions listed in Table 1 were prepared, and powdered devitrified glasses were held at temperatures between 1502°C and 1430°C for 8 or 48 hours. Coarse-grained, euhedral crystals of Fo_{ss} and Mo_{ss} embedded in glasses were found in the quenching runs and were analyzed with an electron microprobe. The microprobe technique is capable of determining the compositions of crystals *in situ* with high precision, and it is considered better than any current X-ray or optical method. The operating conditions of the microprobe and the procedures for the reduction of data were described elsewhere (Yang and Foster, 1972). Ten crystals of Mo_{ss} and five of Fo_{ss} were analyzed in each quenching run for Mg, Ca, and Si. The range of these analyses is reported in Table 1, together with other experimental data.

Results and Discussion

The Fo_{ss} crystallized at 1481°C in two quenching runs of 8 and 48 hours respectively are virtually identical in composition, as are the Mo_{ss} crystallized in the same runs. This suggests that apparent equilibrium can be obtained within a few hours when

TABLE 1. Quenching Experiments and the Compositions of Forsterite and Monticellite Solid Solutions

Compositions (wt %)			Temperature (°C)	Duration (hours)	Compositions of Crystalline Phases*	
SiO ₂	MgO	CaO			wt % Mo in Fo_{ss}	wt % Fo in Mo_{ss}
43.8	23.3	32.9	1440	8	13.5-14.5	16.2-18.0
41.0	29.0	30.0	1496	8	17.2-18.7	27.2-28.7
			1481	8	16.9-17.3	23.5-25.5
			1481	48	15.5-17.5	23.8-24.8
			1463	8	14.0-15.5	20.6-23.0

* Substantial amounts of glass were present in all quenching runs.

Fo_{ss} or Mo_{ss} crystallizes from the melts.

As observed by others during investigation of the metastable crystallization of periclase, the quenching runs at 1463°C, 1481°C, and 1496°C (Table 1) contain a few crystals of periclase in addition to Fo_{ss} and Mo_{ss} . Note that the crystallization of metastable periclases does not necessarily affect the equilibrium compositions of coexisting Fo_{ss} and Mo_{ss} in this study. Contrarily, it might cause their compositions to depart from that of the starting material in cases when the starting compositions used by previous investigators were on the Fo-Mo join and in the single-phase field.

The solvi here observed between 1440° and 1496°C in the system Fo-Mo (Fig. 1) show a forsterite limb very close to that given by Biggar and O'Hara (1969). However, the monticellite limb differs in position and in slope from those reported by the other investigators.

Conclusion

The solvi in the system forsterite-monticellite could better be determined with the method used in the present study. Further application of this method to determine the subsolidus phase relations or the compositions of complex solid solutions for the other systems is therefore encouraged.

Note Added in Proof. R. Warner reinvestigated Fo_{ss} recently and found a limit of 19 wt percent Mo in Fo_{ss} near 1450°C at atmospheric pressure (Warner, personal communication).

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Apatite Chemistry and Phosphorus Fugacity in a Differentiated Igneous Intrusion: Correction

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Values of $\Delta G_r^\circ/2.303 RT$ for two reactions given by Nash (1972) are incorrect.

For the reaction $\text{Ca}_5(\text{PO}_4)_3\text{OH} + 5/2 \text{Mg}_2\text{SiO}_4 + \text{KFe}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2 + 1/2 \text{KAlSi}_3\text{O}_8 + 15/2 \text{SiO}_2 = 5 \text{CaMgSi}_2\text{O}_6 + 3/2 \text{Fe}_2\text{SiO}_4 + 3/2 \text{KAlSi}_2\text{O}_6 + 15/4 \text{O}_2 + 3/2 \text{H}_2\text{O} + 3\text{P}$ the correct value is

$$\frac{\Delta G_r^\circ}{2.303 RT} = \frac{168,508}{T} - 57.87(\pm 7.2).$$

For the reaction $\text{Ca}_5(\text{PO}_4)_3\text{OH} + 3 \text{MgAl}_2\text{O}_4 + 57/4 \text{SiO}_2 + 15/2 \text{Fe} = 15/4 \text{Fe}_2\text{SiO}_4 + 1/2 \text{Mg}_2\text{SiO}_4 + 2\text{CaMgSi}_2\text{O}_6 + 3\text{CaAl}_2\text{Si}_2\text{O}_8 + 1/2 \text{H}_2\text{O} + 3\text{P}$ the correct value is

$$\frac{\Delta G_r^\circ}{2.303 RT} = \frac{51,529}{T} - 20.65(\pm 6.9).$$

The calculated phosphorus fugacities are shifted to higher values of f_p . The equilibrium curves for these two reactions (Nash, 1972, Fig. 1) are shifted, respectively, by the values $\Delta \log f_p = 5478/T +$

$5.26 (\pm 2.4)$ and $\Delta \log f_p = 2730/T + 7.93 (\pm 2.3)$. It is clear, upon recalculation, that the effects of oxidation state and silica activity on the equilibria are not immediately evident, as previously thought. Although the data of Stormer and Carmichael (1971) indicate a decrease of phosphorus fugacity with decreasing magmatic silica activity, no such simple behavior is indicated by the new curve for Shonkin Sag laccolith which crosses theoretical basalt and rhyolite curves. Contrary to prior conclusions, reduction in oxygen fugacity apparently increases phosphorus fugacity values, as indicated by the equilibria for a basaltic assemblage coexisting with metallic iron.

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