

Calcium content of forsterite coexisting with silicate liquid in the system $\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$

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Abstract

The calcium contents of forsterite crystals equilibrated with silicate melts in the system $\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ at 1 atm and 1250°–1450°C were determined by electron microprobe. Over the range of temperatures studied and for melts containing 1.3–18 weight percent CaO, the Ca content of olivine was found to depend linearly upon Ca concentration in the liquid, according to the relation

$$\text{wt\% Ca}_{\text{ol}} = 0.0275 \text{ wt\% Ca}_{\text{liq}}$$

When evaluated as a Ca–Mg exchange equilibrium, the Ca distribution data show equally simple systematics: the molar ratio of oxides $(\text{CaO}/\text{MgO})_{\text{ol}}/(\text{CaO}/\text{MgO})_{\text{liq}}$ is essentially constant at any given temperature and varies in log-linear fashion with $1/T$, given by

$$\ln \left[\frac{(\text{CaO}/\text{MgO})_{\text{ol}}}{(\text{CaO}/\text{MgO})_{\text{liq}}} \right] = -1.487 \times 10^4 T^{-1} (\text{K}) + 4.235$$

The simple relationship determined in this study between Ca abundance in olivine and Ca content of coexisting silicate liquid should prove useful in the identification of natural forsteritic olivine crystals that have not equilibrated with their host magmatic liquids.

Introduction

Calcium is a nearly universal minor constituent of natural iron–magnesium olivines, and is usually present at concentrations ranging between 0.01 and one weight percent (Simkin and Smith, 1970). Despite this wide variation, there have been few systematic experimental studies of Ca content of olivine as a function of the variables pertinent to petrogenesis. The simple forsterite–monticellite (Mg_2SiO_4 – CaMgSiO_4) join has been thoroughly investigated at 1 atm pressure (Ricker and Osborn, 1954; Yang, 1973; Warner and Luth, 1973), and subsolidus compositional data on coexisting forsterite and monticellite are available for pressures up to 10 kbar (Warner and Luth, 1973). In addition, Finnerty (1977) measured Ca concentrations in olivines coexisting with garnet, orthopyroxene, and clinopyroxene at P – T conditions up to 40 kbar and 1400°C. Aside from a small amount of data for basaltic compositions (Leeman, 1974; Roeder, 1974), however, no experimental results on Ca content of olivine coexisting with complex silicate melts have been published. This paper

presents data on Ca concentration in forsterite equilibrated with liquids in the system $\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ at 1 atm and 1250°–1450°C.

Experimental system and methods

The overall plan was to make several isothermal series of runs in which liquid composition was the sole variable. (It was hoped that in so doing it would be possible to separately evaluate the effects of melt composition and temperature upon Ca content of forsterite.) The experimental conditions and bulk compositional information are given in detail by Watson (1977). In brief, the “base” join used was forsterite–albite–anorthite—about half of the liquids coexisting with forsterite lie in this join. Most of the remaining liquid compositions contain a 35 percent excess of CaO relative to liquids in forsterite–albite–anorthite (see Fig. 1). Two of the melts are synthetic iron-free “basalts,” differing from natural basalts only in that Fe was replaced by Mg. In most of the runs at 1250 and 1300°C and occasionally in higher-temperature runs, a second solid phase (spinel or

plagioclase) coexists with forsterite and liquid (see Watson, 1977, Table 2). All bulk compositions were selected to yield 5 to 30 percent total crystals at run temperature.

The runs were made in a platinum-wound, vertical-tube furnace with temperature measurement and control accurate to better than $\pm 2^\circ\text{C}$. The experimental materials (~ 20 mg oxide mix for each run) were contained in platinum capsules that were welded shut to prevent Na volatilization. Run durations ranged from 2 days for experiments at 1450° to 5 days at 1250°C .

Quenched glass compositions were determined with the M.I.T. automated M.A.C. electron microprobe, operating at 15 kV accelerating potential and $0.025 \mu\text{A}$ sample current (see Table 1a of Watson, 1977, for analyses). The sample current was increased to $0.045 \mu\text{A}$ for analysis of Ca in the olivines, and a detailed examination of the $\text{CaK}\alpha$ X-ray peak was made for each run. Background count rates were measured at offset positions on either side of the peak, and extended (30–100 sec) count times were used on the peak itself. Background values determined by the offset method were confirmed by counting at the Ca peak position on spectroscopically pure synthetic forsterite. In each charge, replicate analyses for Ca were made on 10 randomly-selected olivine crystals. Raw count data were reduced with Albee-Ray (1970) correction factors.

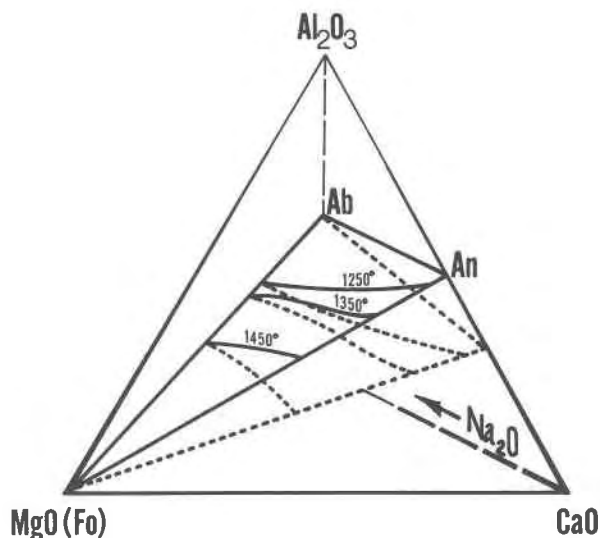


Fig. 1. Schematic diagram illustrating compositional relations among liquid components other than SiO_2 in forsterite/liquid Ca equilibration experiments. Runs were made along 1450° , 1350° , 1300° , and 1250°C isotherms in the two internal planes shown [see text for explanation and Watson (1977) for actual glass analyses].

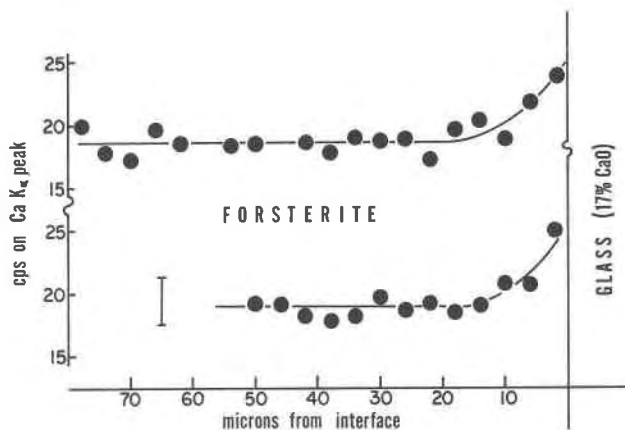


Fig. 2. Electron microprobe traverses on high-purity forsterite crystals approaching the interface with Ca-rich glass (at right). Background count rate is ~ 18 cps; increased count rate near interface results from secondary fluorescence of Ca in glass (see text). Error bar (4 sigma long) shows probable X-ray counting error.

In view of the small size ($10\text{--}70 \mu\text{m}$) and low Ca contents of the forsterite crystals in these runs, a study was made to determine the importance of secondary fluorescence of Ca in adjacent glass by primary X-rays from olivine under the electron beam. For this purpose, a sample of Ca-free synthetic forsterite was embedded in glass (17 weight percent CaO) by heating a coarsely-ground mechanical mixture of the two materials at 1350° for 1 min. During this brief heating period, the molten glass wetted the pure forsterite crystals, thus creating sharp interfaces between Ca-rich glass and Ca-free forsterite. The magnitude of secondary fluorescence contributions to apparent Ca count rates on olivine was examined by traversing pure forsterite crystals with a $\sim 3\text{-}\mu\text{m}$ electron beam in a direction normal to the forsterite/glass interface. At a distance of about $15 \mu\text{m}$ or less from the glass, Ca X-rays were detectable above background (Fig. 2). This finding is taken into account in reporting the analytical results (apparent Ca distributions in runs containing olivine crystals smaller than $30 \mu\text{m}$ are not considered accurate), but because of the variability in crystal size of any given charge, no attempt was made to quantitatively correct for secondary fluorescence.

Although none of the results reported in this paper represent proven equilibrium, several lines of evidence suggest that a close approach to equilibrium was achieved: (1) the Ca contents of olivine crystals in any given run are extremely consistent—the standard deviations of 10 analyses are close to those predicted from X-ray counting statistics (Table 1); (2) by

Table 1. Summary of calcium analyses for experimental runs

Run no.	T, °C	Ca in olivine			Ca in liq (wt%)	
		x-ray peak/BG	Total cts above BG	Std dev, % (10 pts)	Wt %	
OIB4	1250	5.47	1771	3.9	0.338	6.68
MAR4	1250	6.18	2051	5.3	0.392	8.78
3j	1250	2.96	774	7.3	0.148	3.30
4e	1250	2.78	704	12.3	0.134	3.64
6f	1250	3.17	859	7.4	0.164	5.60
7g	1250	5.61	1825	7.4	0.348	8.56
9e	1250	7.98	2762	5.3	0.527	12.64
5e	1250	4.06	1210	7.0	0.231	6.12
3g	1300	2.31	1734	8.3	0.104	3.16
4d	1300	2.26	1656	5.7	0.100	3.57
5f	1300	3.08	824	5.9	0.165	5.70
6e	1300	2.64	649	6.1	0.130	5.59
8e	1300	3.09	829	5.1	0.166	7.53
9j	1300	4.95	1564	5.0	0.314	10.86
2b	1350	1.54	713	14.2	0.043	1.10
3d	1350	2.31	865	5.6	0.104	2.89
4b	1350	2.12	738	7.1	0.089	3.11
5d	1350	3.08	823	4.5	0.165	5.32
6c	1350	2.68	664	6.4	0.133	5.08
7j	1350	3.90	1149	3.8	0.230	7.88
8c	1350	3.08	822	3.8	0.165	6.77
9l	1350	4.68	1456	2.9	0.292	10.28
10b	1350	3.92	1157	4.3	0.232	9.02
2a	1450	1.39	511	17.7	0.029	0.92
3f	1450	1.96	1270	7.3	0.072	2.40
4a	1450	1.93	1223	5.8	0.070	2.57
5c	1450	2.69	1119	5.9	0.128	4.48
6a	1450	2.45	955	2.9	0.109	4.23
7f	1450	3.67	1056	4.2	0.201	6.61
9c	1450	4.91	1550	3.1	0.295	8.67
10a	1450	3.74	1083	3.2	0.206	7.34

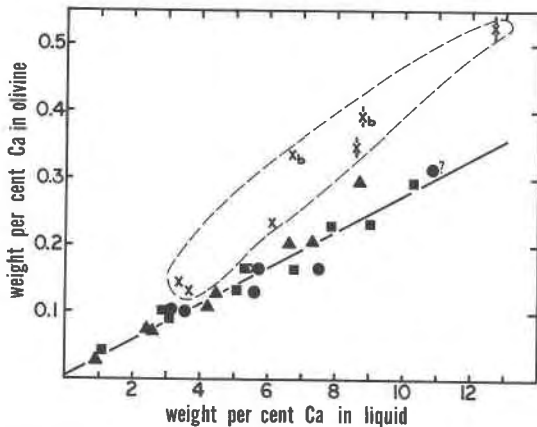


Fig. 3. Calcium content of olivine as a function of Ca concentration in coexisting liquid. Symbols: triangles—1450° runs; squares—1350° runs; circles—1300° runs; X's—1250° runs; b's—iron-free "basalts." The 1250° data points (enclosed in dashed line) are not reliable because of secondary fluorescence effects (see text, Fig. 2). The 1300° point accompanied by a question mark may be unreliable, too, in view of its position on Fig. 4 and the sub-30 μ m size of some of the analyzed forsterite crystals. The line is a least-squares fit to all but the 1250° data, and is given by $Ca_{ol} = 0.0275 Ca_{liq} + 0.0043$. Error bars, usually encompassed by the data points, show variance among 10 separate microprobe analyses (\pm standard errors).

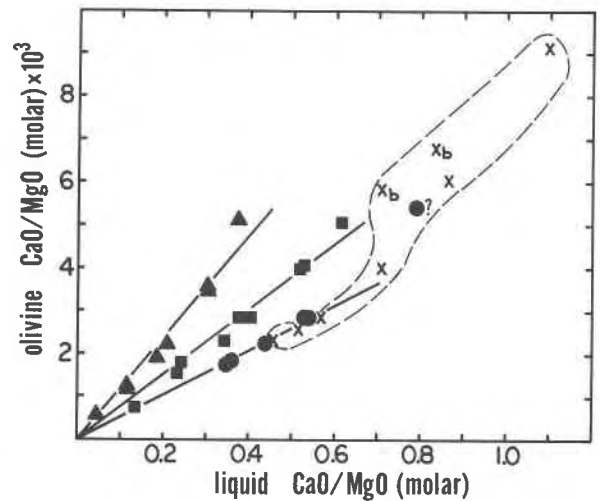


Fig. 4. Molar CaO/MgO in olivine vs. molar CaO/MgO in coexisting silicate liquid. All symbols the same as in Fig. 3. Lines are least-squares fits to constant-temperature data that have been constrained to pass through the origin. Unconstrained least-squares fits give the following lines: 1300°: $Y = 5.98 \cdot 10^{-3} X - 0.35 \cdot 10^{-3}$; 1350°: $Y = 8.74 \cdot 10^{-3} X - 0.49 \cdot 10^{-3}$; 1450°: $Y = 13.24 \cdot 10^{-3} X - 0.35 \cdot 10^{-3}$, where $Y = CaO/MgO$ in olivine and $X = CaO/MgO$ in liquid.

means of duplicate runs varying in duration, the olivines are shown to be equilibrated with the liquids in terms of Mn content (Watson, 1977); and (3) in separate re-equilibration experiments involving Ni, it was found that equilibrium could be attained with respect to Ni in run times similar to those used in the present study (Hart and Davis, 1978).

Results

Calcium contents of 31 olivines coexisting with various $Na_2O-CaO-MgO-Al_2O_3-SiO_2$ melts are presented in Table 1, and selected plots are made in Figures 3–5. Several recent papers (e.g. Banno and Matsui, 1973; Drake and Weill, 1975; Longhi *et al.*, 1976; Watson, 1977) have discussed possible thermodynamic and melt-structure models that can be used to interpret solid/liquid element distribution data. There is no need for review of these models here, and no particular interpretation is favored for the present results. It should only be noted that the silicon:oxygen parameter used by Watson (1977) to describe the melt-composition dependence of forsterite/liquid partition coefficients for Mn is not considered applicable to Ca distributions. Unlike Mn, calcium is a major constituent of the melts whose concentration directly affects melt structure.

In Figure 3, the data are plotted to show the linear

dependence of Ca concentration in olivine upon Ca content of the liquid. Over a temperature interval of 200°C (1250°–1450°) and with gross changes in liquid composition, most of the data points fall close to a line of slope [*i.e.*, (weight percent Ca in forsterite)/(weight percent Ca in glass)] = 0.028. In light of the secondary fluorescence experiment described earlier in this paper, the 1250° data points circled in Figure 3 are regarded as unreliable—all of them represent runs in which the majority of olivine crystals are smaller than 30 μm in diameter. The apparent upward displacement of these points from the general trend of the data would result from a secondary fluorescence contribution to Ca count rates on olivine.

In Figure 4, the data are re-plotted on a diagram similar to that used by Roeder and Emslie (1970) to represent Fe–Mg equilibrium between olivine and liquid. A major difference between Fe–Mg and Ca–Mg olivine/liquid equilibrium is revealed in this figure: the multi-temperature data of Roeder and Emslie fall on a single line of slope (*i.e.*, K_D) = 0.30, while in Figure 4 the slope clearly varies with temperature. Again, if the encircled 1250° data points are disregarded because of probable secondary Ca fluorescence effects, then three distinct, constant-temperature (1450°, 1350°, 1300°) trends remain. When plotted vs. reciprocal absolute temperature, the logarithms of the slope values (K_D 's) fall on a line (Fig. 5).

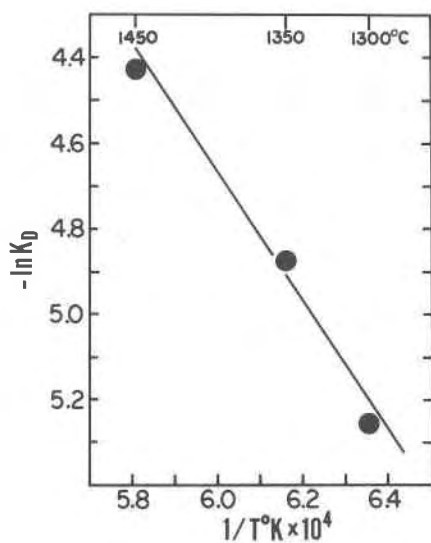


Fig. 5. $\ln K_D$ vs. reciprocal absolute temperature, where K_D = molar $(\text{CaO}/\text{MgO})_{\text{olivine}}$ /molar $(\text{CaO}/\text{MgO})_{\text{liquid}}$. The line is given by $\ln K_D = -1.487 \times 10^4 T^{-1} (\text{K}) + 4.235$.

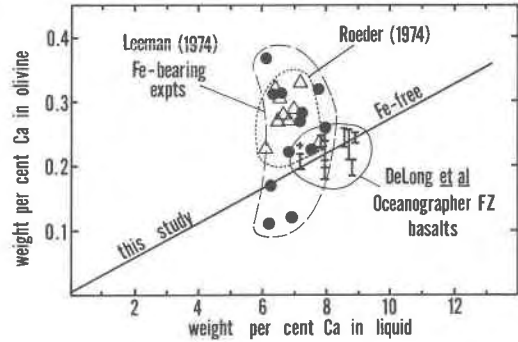


Fig. 6. Experimental data of Leeman (1974) and Roeder (1974) on Ca distribution between Mg–Fe olivine and basaltic liquid compared with Fe-free system trend of the present study (line from Fig. 3). Also plotted are unpublished data of DeLong *et al.* for tholeiitic basalts of the Oceanographer Fracture Zone.

Petrologic applications

Direct, quantitative application of the present results to rocks is precluded by the fact that iron was not included in the system studied. Inspection of the experimental data of Leeman (1974) and Roeder (1974) reveals that iron-bearing olivines coexisting with basaltic liquids contain Ca at levels generally predicted by the present study (Fig. 6). However, even for the relatively small range in Ca content of the liquids used by these workers, considerable scatter about (and generally above) the well-defined “iron-free” line is obvious. Furthermore, on a plot similar to Figure 4 (but with MgO replaced by MgO + FeO), calcium in iron-bearing olivines shows no systematic dependence upon temperature and some positive correlation with iron content. Thus, unless secondary fluorescence has contributed to the scatter of data points for iron-bearing compositions (the studies of Leeman and of Roeder were not specifically aimed at Ca distribution), it seems likely that calcium substitution is more extensive in iron-rich olivines than in forsterite, as suggested by Warner and Luth (1973). For this reason, any petrogenetic conclusions based upon the data presented in this paper should be confined to forsteritic olivines.

Notwithstanding the effect of small amounts of iron, it seems clear from Figure 3 that the level of calcium in an igneous olivine should be directly proportional to, and dominantly determined by, the calcium content of the host magmatic liquid. Any dependence of calcium abundance in olivine upon SiO_2 activity in the melt (Stormer, 1973) is apparently minor (Fig. 7) and/or is obscured by other effects. For rocks of generally basaltic composition, a relatively

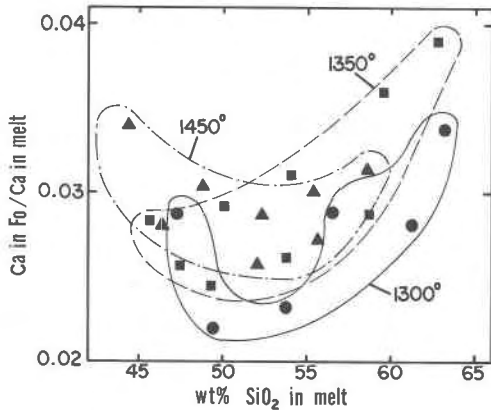


Fig. 7. Distribution of Ca between forsterite and liquid plotted against SiO_2 content of the liquid. Symbols as in Fig. 3; 1250° data points excluded.

small range in calcium content of phenocrystic olivine is predicted. According to Figure 3, for example, olivine crystals in equilibrium with alkali basaltic liquids containing 8–10 weight percent CaO should have ~0.16–0.20 weight percent dissolved Ca; olivines of more calcic oceanic-ridge tholeiites or melilite-bearing rocks should have somewhat higher Ca values (up to 0.30 weight percent). Insofar as these predictions can be tested by available analytical data, they are borne out by observed Ca abundances in extrusive-rock olivines. Unpublished data of DeLong *et al.* on tholeiitic basalts from the Oceanographer Fracture Zone, for example, plot exactly on the present iron-free calibration line (Fig. 6). In addition, the average Ca content of 76 olivines in host rocks broadly designated “basalt” in the study of Simkin and Smith (1970) is 0.20 weight percent (*i.e.*, the predicted value for olivines in equilibrium with liquids containing 10 weight percent CaO). The highest Ca abundances measured in that study were in olivines from melilite-bearing mafic extrusive rocks, although the observed levels (0.38–1.07 percent) are considerably higher than those predicted by the experimental data.

The most useful application of the results reported in this paper may be in identifying olivine crystals that have *not* equilibrated with their host liquids. Four of the five olivine crystals designated “xenocryst” or “large single crystal” in the study of Simkin and Smith (1970) contain less Ca than would be predicted for olivines coexisting with the generally basaltic host liquids indicated. Three of these crystals, in fact, are apparently low in Ca by an order of magnitude, which would appear to confirm that they are

indeed xenocrysts. Perhaps by virtue of their original coexistence with orthopyroxene and/or clinopyroxene in the upper mantle, these olivines contain relatively low concentrations of Ca (Warner and Luth, 1973; Finnerty, 1977), and have not re-equilibrated with the melt that entrained them. The low Ca contents of two melilite basalt olivines [0.05 and 0.07 weight percent, analyses 9 and 10 of Simkin and Smith (1970)] can be explained in a similar manner.

As a further application of Figure 3, it may be possible in some cases to distinguish cumulate from non-cumulate olivines on the basis of Ca concentration. Picrites and troctolites, for example, show a broad range in Ca content of their olivines [0.00–0.35 weight percent (Simkin and Smith, 1970)]; those with low-Ca olivines might be interpreted as directly-crystallized, low-Ca, high-Mg magmas, while those containing olivines whose Ca concentrations would result from equilibrium with basaltic liquid can be regarded as cumulates from a basaltic magma.

Concluding remarks

Molar volume data have been used to show that Ca abundance in olivine should be negatively correlated with pressure (Stormer, 1973). This predicted effect is substantiated by the observed broadening of the forsterite–monticellite solvus (Warner and Luth, 1973) and the slight decrease in Ca content of olivine coexisting with garnet, orthopyroxene, and clinopyroxene (Finnerty, 1977) at high pressures. However, the magnitude of any pressure effect on Ca content of olivine coexisting with silicate melt and other basaltic phases is unknown. The present study has shed no light on the effect of pressure, but inasmuch as Ca content of olivine is sensitive to differences in Ca content of coexisting melt (Fig. 3), no conclusions regarding pressure of crystallization should be drawn without knowledge of Ca abundance in the host magma and, ideally, its evolution through time. This paper provides systematic experimental data that may be useful in the isolation of actual pressure effects in future experiments.

Finally, it should be noted that the distribution of Ca between olivine and coexisting melt holds considerable promise as a geothermometer. This aspect was not emphasized in the present report because the possible influence of iron was not investigated, but it is clear from Figures 4 and 5 that Ca–Mg exchange between olivine and liquid is quite sensitive to changes in temperature and is unaffected by extensive variation in bulk melt composition. These com-

bined characteristics hold for few available exchange-equilibrium geothermometers.

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