

Olivine-Liquid Equilibrium

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Abstract. A number of experiments have been conducted in order to study the equilibria between olivine and basaltic liquids and to try and understand the conditions under which olivine will crystallize. These experiments were conducted with several basaltic compositions over a range of temperature (1150–1300° C) and oxygen fugacity ($10^{-0.68}$ – 10^{-12} atm.) at one atmosphere total pressure. The phases in these experimental runs were analyzed with the electron microprobe and a number of empirical equations relating the composition of olivine and liquid were determined. The distribution coefficient

$$K_D = \frac{(X_{\text{FeO}}^{\text{Ol}})}{(X_{\text{FeO}}^{\text{Liq}})} \frac{(X_{\text{MgO}}^{\text{Liq}})}{(X_{\text{MgO}}^{\text{Ol}})}$$

relating the partitioning of iron and magnesium between olivine and liquid is equal to 0.30 and is independent of temperature. This means that the composition of olivine can be used to determine the magnesium to ferrous iron ratio of the liquid from which it crystallized and conversely to predict the olivine composition which would crystallize from a liquid having a particular magnesium to ferrous iron ratio.

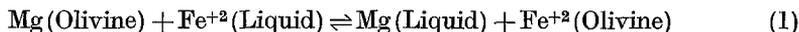
A model (saturation surface) is presented which can be used to estimate the effective solubility of olivine in basaltic melts as a function of temperature. This model is useful in predicting the temperature at which olivine and a liquid of a particular composition can coexist at equilibrium.

Introduction

Olivine is the first or an early crystallizing phase from basalts of quite different composition, as observed in nature and as determined by experimental studies. Early experiments of Bowen and Schairer (1935) in the MgO–FeO–SiO₂ system demonstrated that there is complete solid solution between forsterite and fayalite, and that in most parts of the system the olivine is richer in magnesium and poorer in iron than the coexisting melt.

The present work relates the compositions of coexisting olivine and basaltic melt as a function of temperature. Knowledge of this relationship permits testing of natural olivine–liquid pairs for equilibration and allows a clearer understanding of paths of equilibrium and fractional crystallization in basaltic magmas.

The distribution of magnesium and ferrous iron between olivine and liquid can be represented by the following equation:



where Mg(Olivine) refers to magnesium in olivine and Fe⁺²(Liquid) refers to the ferrous iron in the liquid phase. An equilibrium constant (*K*) for this reaction

can be written in terms of the activities (a) of the various chemical species, i. e. (Mg^{+2} , MgO , $\text{MgSi}_{0.5}\text{O}_2$) in the liquid and solid solution or in terms of the mole fraction (X) and activity coefficients (γ) of the various species:

$$K = \frac{(a_{\text{FeO}}^{\text{Ol}})}{(a_{\text{FeO}}^{\text{Liq}})} \frac{(a_{\text{MgO}}^{\text{Liq}})}{(a_{\text{MgO}}^{\text{Ol}})} = \frac{(X_{\text{FeO}}^{\text{Ol}})}{(X_{\text{FeO}}^{\text{Liq}})} \frac{(X_{\text{MgO}}^{\text{Liq}})}{(X_{\text{MgO}}^{\text{Ol}})} \times \frac{(\gamma_{\text{FeO}}^{\text{Ol}})}{(\gamma_{\text{FeO}}^{\text{Liq}})} \frac{(\gamma_{\text{MgO}}^{\text{Liq}})}{(\gamma_{\text{MgO}}^{\text{Ol}})}. \quad (2)$$

The ratio of the mole fractions in Eq. (2) is defined in the present study as the distribution coefficient. For example:

$$K_D = \frac{(X_{\text{FeO}}^{\text{Ol}})}{(X_{\text{FeO}}^{\text{Liq}})} \frac{(X_{\text{MgO}}^{\text{Liq}})}{(X_{\text{MgO}}^{\text{Ol}})} \quad (3)$$

The equilibrium represented by Eq. (1) was experimentally investigated by Bowen and Schairer (1935) in their study of the Mg_2SiO_4 – Fe_2SiO_4 system. Bowen and Schairer presented thermodynamic equations which expressed the change in the freezing point of forsterite and fayalite in terms of the temperature and heat of fusion of these compounds. These equations were revised and a heat capacity term was introduced by Bradley (1962). Two of the equations derived by Bradley are as follows:

$$\log_{10} \frac{X_{\text{Fay}}^{\text{Ol}}}{X_{\text{Fay}}^{\text{Liq}}} = -1550 \left(\frac{1}{1478} - \frac{1}{T} \right) - 1.887 \log_{10} \left(\frac{T}{1478} \right) \quad (4)$$

$$\log_{10} \frac{X_{\text{For}}^{\text{Ol}}}{X_{\text{For}}^{\text{Liq}}} = -1420 \left(\frac{1}{2163} - \frac{1}{T} \right) - 1.887 \log_{10} \left(\frac{T}{2163} \right). \quad (5)$$

Where $X_{\text{For}}^{\text{Ol}}$ represents the mole fraction of forsterite ($\text{MgSi}_{0.5}\text{O}_2$) in the olivine solid solution and $X_{\text{Fay}}^{\text{Liq}}$ represents the mole fraction of fayalite ($\text{FeSi}_{0.5}\text{O}_2$) in the liquid solution. Bradley found that the phase diagram for the forsterite–fayalite system calculated from Eqs. (4) and (5) was the same as the experimentally determined phase diagram of Bowen and Schairer (1935). Thus the use of mole fraction or concentration of iron and magnesium instead of activity for the olivine–liquid equilibrium is justified for the forsterite–fayalite system, and the liquid and solid solution in this system can be considered ideal at high temperatures. Any deviation of the liquid or solid solution from ideality (Nafziger and Muan, 1967) is either too small to affect the calculations significantly or the ratio of the mean activity coefficients is close to unity (Bradley, 1962). By subtracting Eq. (5) from (4) and combining terms, we can determine the variation of the distribution coefficient of Eq. (1) as a function of temperature:

$$\log K_D = \frac{130}{T} - 0.7044 \quad (6)$$

where $K_D = K$ for the forsterite–fayalite system. The small numerator for the temperature term in Eq. (6) is due to the similar heats of fusion of forsterite and fayalite, and as a result the variation of K_D as a function of temperature is small at high temperatures.

In the present study the equilibrium represented by Eq. (1) has been determined for olivine and basaltic liquid, and equations similar to (4), (5) and (6) have been determined from phase equilibrium studies on three natural basalts at controlled oxygen fugacities and temperatures from 1150 to 1300° C.

Experimental Technique

The glass starting materials used in the experimental runs were prepared by the repeated (twice) fusion and grinding of three natural basalts described in Table 1. Ten different basaltic glasses were tested, but only with these three basalts did olivine crystallize by itself over a range of temperature and oxygen fugacity. The experimental charges were placed in crucibles selected to minimize reaction with the charges at the temperatures and oxygen fugacities (f_{O_2}) of the experiments. Above an f_{O_2} of 10^{-3} atmospheres, platinum sheet was used for crucibles; between 10^{-3} and 10^{-9} atmospheres, two different silver-palladium alloys (60 Ag:40 Pd and 55 Ag:45 Pd) were used depending on the temperature and f_{O_2} . Below an f_{O_2} of 10^{-9} atmospheres and at high temperatures, alumina crucibles were used. The amount of iron loss to the metal crucibles and the alumina gain from the alundum crucibles was generally less than 10 per cent of the amount present as shown by the probe analyses and the iron analyses of the liquid phase. The oxygen fugacity was controlled by gas mixtures of carbon dioxide—hydrogen and air—argon, using standard mixing techniques (Darken and Gurry, 1945). The log of f_{O_2} is believed to be accurate to within ± 0.05 as determined by calibration with Fe-FeO and Ni-NiO, (Campbell and Roeder, 1967) and the temperature in the furnace is believed to be accurate to $\pm 4^\circ$ C as determined by Pt-Pt90Rh10 thermocouples calibrated at the melting points of gold and diopside. The samples were quenched in the gas atmosphere at the top of the furnace after at least two days at the desired temperature and f_{O_2} . This amount of time was found to be sufficient for equilibrium and confirmed the results of Kennedy (1948), Yoder and Tilley (1962), Fudali (1965) and Hill (1969).

In order to determine the oxidation state of iron and to check for the possible loss of iron from the sample to the crucible, a portion of each sample was analyzed for FeO and Fe_2O_3 by L. Mes using the technique described by D. Presnall (1966). Another portion of each sample was mounted for electron microprobe analyses of the olivine crystals and the quenched liquid phase. The probe analyses were carried out with an ARL-AMX probe at 15 kv and sample currents of 0.05 and 0.1 microamps using a beam of approximately one micron diameter. The olivine crystals were analyzed for iron and magnesium and the composition of the olivine was found using calibration curves determined with olivine standards very kindly supplied by C. Smith, Geological Survey of Canada, and B. Evans, University of California, Berkeley.

The olivine crystals in mixture GI-654 (7-11) were analyzed by the probe for calcium, nickel, and manganese, in addition to iron and magnesium. The analysis gave 80.6% Mg_2SiO_4 , 18.0% Fe_2SiO_4 , 0.41% Ca_2SiO_4 , 0.57% Ni_2SiO_4 , and 0.25% Mn_2SiO_4 . The runs listed in Table 2 show only the forsterite and fayalite content of the olivine; thus the total for the olivine analysis is generally less than 100%. The glass surrounding the olivine crystals was

Table 1. Glass analyses

	GI-654	GI-C218	GI-C71
SiO ₂	49.6	47.9	47.3
Al ₂ O ₃	12.2	13.8	11.8
Fe as Fe ₂ O ₃	12.7	12.8	12.5
MgO	10.2	8.2	10.8
CaO	10.0	11.4	11.3
Na ₂ O	2.2	2.5	2.0
K ₂ O	0.58	0.74	0.62
TiO ₂	2.8	2.1	2.4
	100.3	99.4	98.8
Rock collected by:	D.H. Richter	G.A. MacDonald	G.A. MacDonald
Location	Kilauea, Hawaii	Hualalai, Hawaii	Hualalai, Hawaii
Rock name	olivine basalt	Alkali olivine basalt	Ankaramite

Table 2. *Experimental results*

	Gl-654	Gl-654	Gl-654	Gl-654
No.	A-1	7-3	9-2	11-2
log f_{O_2}	-0.68	-6.94	-9.03	-11.06
Temp. (°C)	1198	1201	1198	1200
Time (hrs)	44	45	44	70
crucible	Pt.	55 Ag	Al ₂ O ₃	Al ₂ O ₃
Total FeO	1.25	8.60	N.D.	10.84
Total Fe ₂ O ₃	10.31	3.40		0.89
Phases	OL + MAG + LIQ	saOL + sa MAG + LIQ	OL + trSP + LIQ	OL + LIQ
Wt.-% Fayalite	N.D.	20	24	26
Wt.-% Forsterite	N.D.	79	73	72
Liquid Composition (Wt.-%)				
SiO ₂	51.2	50.3	50.4	50.9
Al ₂ O ₃	12.8	13.3	14.4	14.0
Fe as Fe ₂ O ₃	10.5	12.4	11.6	11.3
CaO	10.7	10.6	10.9	10.0
MgO	9.5	7.9	6.7	7.1
Na ₂ O	2.2	2.4	2.5	2.5
K ₂ O	0.55	0.65	0.67	0.61
TiO ₂	2.8	3.0	3.1	3.1
Total	100.2	100.6	100.3	99.5

Because of space limitation only four representative examples of the forty-four experiments have been shown. A complete table is available from the senior author.

sa = small amount, tr = trace, OL = Olivine, LIQ = Liquid, MAG = Magnetite, SP = Spinel, ND = not determined.

analyzed with the probe using as standards¹ basaltic glasses which have been analyzed by wet chemical methods and by X-ray fluorescence. Seventeen probe analyses of nine basaltic glasses of known composition gave an average deviation of less than 5% of the amount present for Si, Al, Ti, Fe and Ca, and 6% of Mg, 8% of K, and 9% of Na. Because the range in composition of the glass in the experimental runs is less than that of the nine standards, it is believed that the average deviation for the experimental runs is less than indicated above.

Experimental Results

The results for forty-four experimental runs, including the bulk analysis for FeO and Fe₂O₃, the probe analyses of the olivine crystals, and the probe analysis (Si, Al, Fe, Ca, Mg, Na, K, Ti) of the quenched liquid phase, are available from the senior author. The data for four representative runs are shown in Table 2.

Most of the experiments were conducted with the basalt Gl-654, and in order to appreciate how the phase assemblage changes with f_{O_2} and temperature, the data for this sample are plotted on Fig. 1. The boundaries drawn between different phase assemblages are based on the runs of the present study and also on experimental data discussed in an earlier study of Hill and Roeder (1967) and Hill (1968). The major effect of the variation of f_{O_2} on the crystallization of a basaltic

¹ Samples of these glasses are available from the senior author for probe standards.

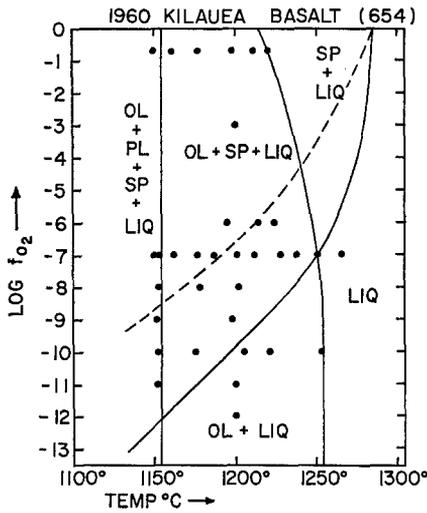


Fig. 1. The distribution of phases for experiments at controlled temperatures and oxygen fugacities for Gl-654

melt is on the temperature of first appearance of spinel and olivine and the composition of the ferromagnesium minerals spinel, olivine, and pyroxene. Although the change in composition and amount of spinel is continuous (Hill, 1968) from low to high oxygen fugacities, the dashed line represents an arbitrary division between what we have called magnetite (black opaque cubes) at higher oxygen fugacities and lower temperatures, and chrome spinel (small reddish cubes with octahedral truncations) at higher temperatures and lower oxygen fugacities. The amount of spinel in the region at higher temperatures and lower oxygen fugacities than the dashed line (chrome spinel) is very small (much less than 1%) as compared to the so-called magnetite region.

The variation in the composition of olivine in Gl-654 as a function of temperature at a constant f_{O_2} of 10^{-7} atmospheres and the variation as a function of f_{O_2} at a constant temperature of $1200 \pm 5^\circ \text{C}$ is shown in Figs. 2a and b. As expected, the olivine is richer in magnesium at higher temperatures and at higher oxygen fugacities. The change in olivine composition as a function of temperature would be even greater if those runs having the same ferrous to ferric ratio were considered (assuming constant total composition crystallization). Fig. 2b shows the fairly large change in olivine composition as a function of $\log f_{O_2}$ at a constant temperature. Those f_{O_2} values where the ferrous and ferric iron in the liquid shows the greatest variation is between 10^{-4} and 10^{-9} atmospheres. At an f_{O_2} higher than this range, little ferrous iron is present, and the equilibrium olivine composition is rich in forsterite, whereas at an f_{O_2} lower than this range but above 10^{-13} atmospheres, most of the iron in the system is ferrous and the olivine is richest in fayalite. Lowering the f_{O_2} below approximately 10^{-13} atmospheres causes reduction of the iron to the metallic state, and thus a more magnesian olivine crystallizes (Hill and Roeder, 1967). The dashed curve is based on the relationship which is expected from the change in the ferrous iron content of the total charge as a function of $\log f_{O_2}$. The relationship between the oxidation

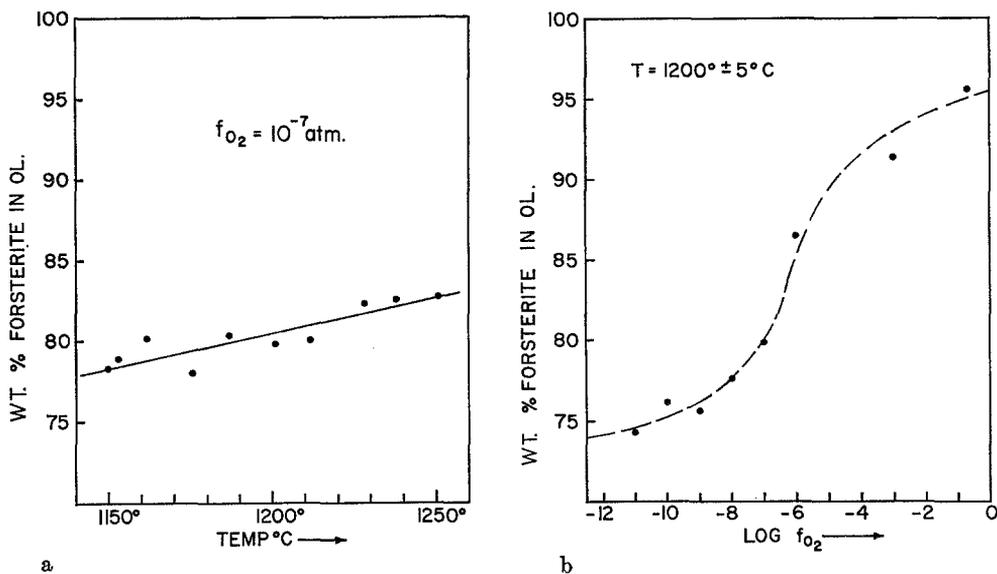


Fig. 2. a The composition of olivine in runs of Gl-654 as a function of temperature at a constant f_{O_2} . b The composition of olivine in runs of Gl-654 as a function of f_{O_2} at a constant temperature

state of iron in the charge and the f_{O_2} is given by the following equation, which was calculated by a least squares refinement² of the data of 1200 ± 5 °C:

$$\log \frac{X_{FeO}}{X_{FeO_{1.5}}} = -0.20 \log f_{O_2} - 1.04.$$

The coefficients for this equation are within the range determined for basalts by Fudali (1965). The effect of oxidation and reduction on the ratio of total iron in olivine over the total iron in the liquid phase is shown by the data plotted in Fig. 3. The dashed curve illustrates how we expect the iron ratio to approach zero exponentially at high oxygen fugacities and a constant number (~ 1.8) at lower oxygen fugacities. The olivine which crystallizes at an f_{O_2} below 10^{-6} atmospheres contains a higher percentage of iron than the liquid, and thus fractional crystallization of olivine under these conditions will result in both magnesium and iron depletion in the liquid phase.

Since one of the purposes of the present study is to relate the composition of olivine, the percentage of MgO and FeO in the liquid and the temperature of olivine crystallization, it is necessary to know the FeO content of the liquid. This could not be determined directly, because the electron microprobe could only determine total iron in the glass phase. The percentage of FeO in the liquid phase was calculated by the following procedure. Assuming olivine and liquid were the only phases present, the percentage of liquid was calculated from the percentage of MgO in the total sample, MgO in the liquid phase, and MgO in the olivine.

² The product moment correlation coefficient for this calculation with eight points is -0.982 .

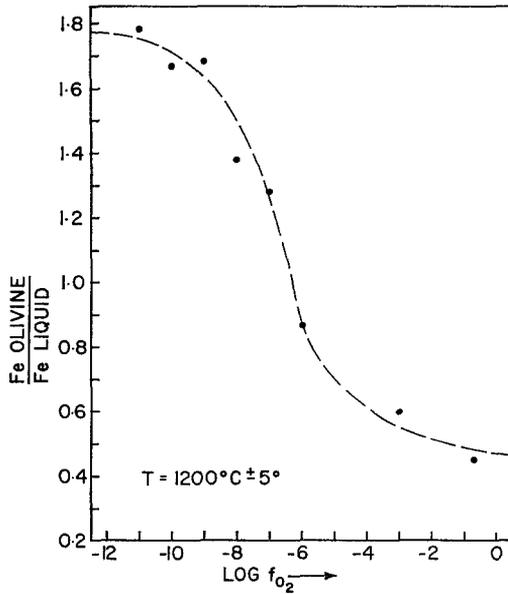


Fig. 3

Fig. 3. The change in the distribution of total iron (weight %) between olivine and liquid as a function of f_{O_2} at a constant temperature

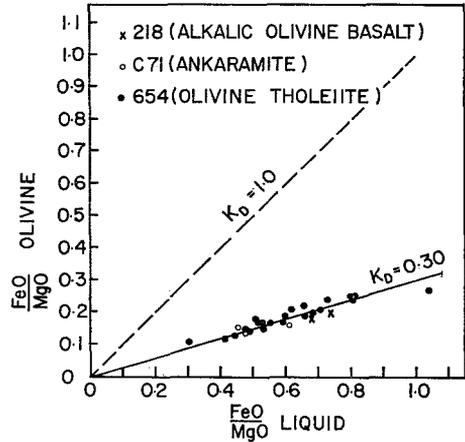


Fig. 4

Fig. 4. The change of the FeO to MgO ratio (mole %) for coexisting olivine and liquid in twenty-seven experimental runs

This percentage of liquid, together with the total iron in the liquid and the ferrous and ferric content of the total sample, could be used to calculate the amount of ferrous iron in the liquid. It was impossible to calculate the FeO content of the liquid at oxygen fugacities greater than 10^{-6} atmospheres because of the presence of a large amount of magnetite of unknown ferrous and ferric iron content. At lower oxygen fugacities, the presence of a small amount of spinel and/or plagioclase does not significantly affect this calculation. The error in the calculated FeO content is believed to be small because there was always more than 85 percent liquid in the runs, and the corrected data for samples run at 10^{-7} and 10^{-8} atmospheres are consistent with those samples run at a low f_{O_2} (10^{-10} to 10^{-12}) in which almost all the iron is ferrous and there is essentially no correction for ferric iron. The MgO and FeO contents were determined for olivine and coexisting liquid (glass) in 27 experiments. The ratio of FeO to MgO in the olivine crystals as a function of the ratio of FeO to MgO in the liquid phase is shown for the 27 runs in Fig. 4. The slope of the line in Fig. 4 is equal to the distribution coefficient (K_D) of Eq. (1), and is the same for the three basalts studied. The distribution for MgO and FeO between olivine and liquid for these same runs is plotted as a function of temperature in Figs. 5a and b. The data for the 27 runs (solid dots) were used to calculate by least squares the Eqs. (11) and (12) for the best fitting straight lines. In addition to the data at one atmosphere total pressure from the present study, we have plotted data (open circles) from high pressure experiments

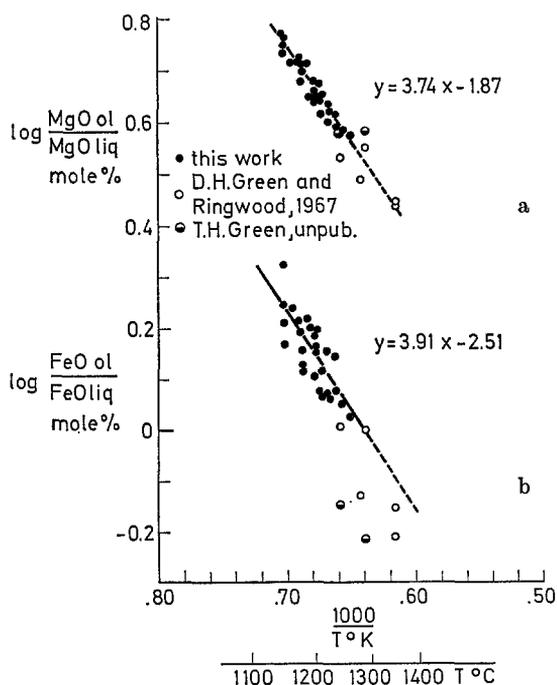


Fig. 5. a The change in the MgO distribution between olivine and liquid as a function of temperature. b The change in the FeO distribution between olivine and liquid as a function of temperature. The equation for the straight lines were calculated from the data represented by the solid dots

described by D. Green and Ringwood (1967), and unpublished data (half-solid circles) kindly supplied by T. H. Green. The high pressure experiments were all run at 4.5 and 9.0 kilobars total pressure and were not included in the data used to calculate Eqs. (11) and (12). The change in the magnesium ratio between olivine and liquid is linear³ over the temperature range of the present study. The greater scatter of the data for the iron ratio as a function of temperature is believed to be mainly due to the problems in calculating the FeO and Fe₂O₃ content of the liquid.

$$\log \frac{X_{\text{MgO}}^{\text{Ol}}}{X_{\text{MgO}}^{\text{Liq}}} = \frac{3740}{T} - 1.87. \quad (11)$$

$$\log \frac{X_{\text{FeO}}^{\text{Ol}}}{X_{\text{FeO}}^{\text{Liq}}} = \frac{3911}{T} - 2.50. \quad (12)$$

$$\log \frac{X_{\text{FeO}}^{\text{Ol}}}{X_{\text{FeO}}^{\text{Liq}}} \frac{X_{\text{MgO}}^{\text{Liq}}}{X_{\text{MgO}}^{\text{Ol}}} = \log K_D = \frac{171}{T} - 0.63. \quad (13)$$

If Eq. (11) is subtracted from Eq. (12), we get an Eq. (13) which represents the change in the distribution coefficient, K_D , as a function of temperature. For the temperature range (1150–1300°C) of the present study the change in K_D as a function of temperature is very small, and is well within the experimental error of the present study. The K_D values determined from the 27 experimental runs

³ The product moment correlation coefficient for the calculation with 27 points for Eq. (11) is 0.97 and for Eq. (12) is 0.80.

vary from 0.26 to 0.36. Using Eq. (13) for extrapolation, we find that the calculated K_D values vary from 0.31 at 1000° C to 0.29 at 1400° C, which is within our experimental error. It should be noted that an analytical error of $\pm 2\%$ forsterite in the determination of the olivine composition can change the K_D value from 0.29 to 0.34.

As explained in the introduction, the K_D values for the olivine-liquid equilibrium calculated using Bradley's equations are essentially independent of temperature ($K_D = 0.25$ at 1000° C and 0.24 at 1400° C) because of the similar heats of fusion of fayalite and forsterite. Thus whether we use the thermodynamic equations for freezing point depression (Bradley) or the empirical equations for basalts (present study) we come to the same conclusion, that the composition of olivine is virtually independent of temperature (and maybe pressure) and depends almost entirely on the ratio of magnesium to ferrous iron in the liquid.

One of the most surprising results of the present experimental study is how closely the classical thermodynamic equation for freezing point depression fits the experimental results for a system as complicated as a basaltic liquid. Although we have used the concentrations of MgO and FeO for Eqs. (11) and (12) the equations would apply to freezing point depression only if we consider a hypothetical olivine species (i.e. Fe_2SiO_4 , $\text{FeSi}_{0.5}\text{O}_2$) in the crystals and coexisting liquid. If there is considerably more SiO_2 in the system than is necessary to combine with the total FeO plus MgO to form olivine, we can consider the equilibrium to be determined mainly by the availability of magnesium and iron. In almost all igneous environments, there is considerably more silica than is necessary to combine with MgO plus FeO to form olivine, and thus the concentrations of MgO and FeO are used in Eqs. (11), (12), and (13).

The experimental and calculated values (using the equations of Bradley) for K_D are within 0.06 units, and the actual and calculated temperature for a particular $\text{Mg}^{\text{ol}}/\text{Mg}^{\text{liq}}$ ratio are within 80° C from 1000° C to 1400° C. Thus the variation in the ratio of silica, iron and magnesium, and the addition of such elements such as calcium, aluminum, sodium, potassium and titanium to liquids of the Mg_2SiO_4 - Fe_2SiO_4 system has only a small effect on the equilibrium represented by Eq. (1). This means that the relative availability of ferrous iron and magnesium in a basaltic liquid is about the same as in the simpler system, and that there are no major complexes in the basaltic melt which are selectively tying up magnesium or ferrous iron. For this reason the distribution coefficient as determined in the present study can be used as a first approximation to represent the equilibrium between olivine and liquid for most liquid compositions to be found in nature. Experimental data on much more iron-rich liquids and over a larger temperature interval will be necessary and are in progress to check the general applicability of the present study.

Petrological Applications

The experimental results of the present study indicate the olivine is richer than the basaltic liquid in both magnesium and ferrous iron. This might not be what would be expected from an examination of the Mg_2SiO_4 - Fe_2SiO_4 system (Bowen and Schairer) where the liquid phase is always richer in FeO than the olivine

with which it is in equilibrium. This difference in behaviour can be illustrated by examining Eq. (4) and Fig. 5b. At all temperatures above the melting point of fayalite (1205° C or 1478° K), the left hand side of Eq. (4) is negative, or the FeO in olivine over the FeO in liquid is less than one. At the melting point of fayalite (1478° K), this ratio is equal to one, while at temperatures below the melting point of pure fayalite, this ratio is greater than one. The data from the present study (Fig. 5b) demonstrate that the logarithm of FeO in olivine over FeO in basaltic liquid is zero at 1280° instead of at 1205° C, and that at temperatures below 1280° C the olivine contains more ferrous iron than the liquid. The change in the *total iron* content of the liquid with fractional crystallization of olivine will depend not only on the temperature but also on the oxygen fugacity during crystallization. Only at oxygen fugacities greater than 10^{-6} at 1200° C (Fig. 3) or at temperatures above 1280° C will the crystallization of olivine cause absolute iron enrichment in the liquid. Under most geological conditions we believe the olivine will be richer than the liquid not only in ferrous iron but also in total iron.

Iron enrichment in the liquid by fractional crystallization can be produced only by the separation of an iron-free or iron-poor phase such as plagioclase. It is probably not fortuitous that production of extreme iron-rich differentiates from basic intrusions has been preceded by crystallization of huge volumes of plagioclase-rich rocks: Skaergaard (Wager and Deer, 1939), Kiglapait (Morse, 1961), Michikamau (Emslie, 1965).

One of the principal conclusions of the present study is that the composition of olivine is independent of temperature and depends only on the ratio of magnesium to ferrous iron in the liquid from which the olivine is crystallizing. Thus the composition of olivine can be used to determine the ratio of magnesium to ferrous iron of the liquid from which the olivine crystallized. This obviously assumes that the composition of the olivine found in nature is due to a liquid-crystal equilibrium, and not a crystal-crystal equilibrium of the kind described by Irvine (1966) for olivine-spinel. Conversely, we can determine the composition of olivine which can coexist with or crystallize from a liquid having a particular ferrous iron to magnesium ratio. This does not mean we can predict *whether* olivine *will* crystallize from a liquid of a particular magnesium to ferrous iron ratio, only that the composition of olivine, *if* it does crystallize, will be of a particular composition. We could also determine whether an olivine of a particular composition could have crystallized from a liquid of a particular magnesium-ferrous iron ratio.

In Fig. 6, we have plotted the olivine composition calculated from the liquid composition for five samples from Kilauea and five experimental runs of natural samples run at high pressure. The correspondence between the calculated and actual forsterite content of olivine is very good for low iron samples, but we have no data for fayalitic olivines.

Medaris (1969) and Williams and Eugster (1969) determined the K_D for magnesium-iron distribution between olivine and calcium-free pyroxene, and found that it is independent of temperature. We have combined this distribution coefficient with the olivine-liquid distribution coefficient determined in the

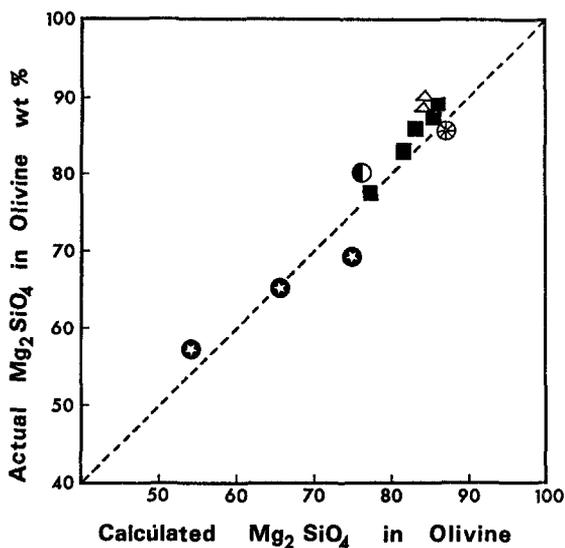
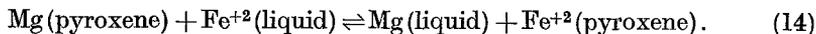


Fig. 6. Actual composition of olivine is compared to the composition which is calculated from the liquid composition using $K_D = 0.30$. The data are from the following sources: (⊛) Moore and Evans (Prehistoric Makaopuhi Lava Lake); (●) Peck, Wright and Moore (Aala Lava Lake, Hawaii); (⊕) Hakli and Wright (Makaopuhi Lava Lake); (△) Green T. (Basalt Experiments 4.5 and 9.0 kb); (■) Green D. and Ringwood (Basalt experiments 4.5 and 9.0 kb)

present study in order to calculate the distribution of magnesium and ferrous iron between calcium free pyroxene and liquid.



The calculated distribution coefficient for the pyroxene-liquid equilibrium [Eq. (14)] is 0.23, as compared to 0.30 for the olivine-liquid equilibrium [Eq. (1)]. The results of Medaris or Williams and Eugster and the present study suggest that the composition of olivine and calcium-free pyroxene can both be used to estimate the magnesium-ferrous iron ratio of the liquid from which they crystallized.

A convenient method of graphically representing the dependence of olivine composition on the composition of the liquid is to plot the mole per cent FeO in the liquid against the mole per cent MgO in the liquid (Fig. 7). The composition of olivine which can coexist with liquids of varying magnesium-ferrous iron ratio is shown by dashed lines radiating from the origin. If the K_D value is independent of temperature and composition, the lines are straight as shown in Fig. 7. If the K_D varies with temperature but is independent of composition, the lines are curved. If the value of K_D is dependent on the composition of the liquid, the relationship is too complicated for a simple graphical representation. The lines of constant olivine composition in Fig. 7 have been drawn using the K_D value determined in the present study. We have also shown isothermal lines on Fig. 7. These isothermal lines represent a projection of the saturation surface (liquidus surface) for olivine, assuming that the equations for freezing point depression [Eqs. (11) and (12)] as determined in the present study are valid for the range of temperature and composition under consideration. As stated earlier, we have assumed that there is more than enough SiO_2 in the liquid to combine with MgO and FeO to form olivine. This saturation surface could also be calculated using the equations of Bradley [Eqs. (3) and (4)]; however, it would then be necessary

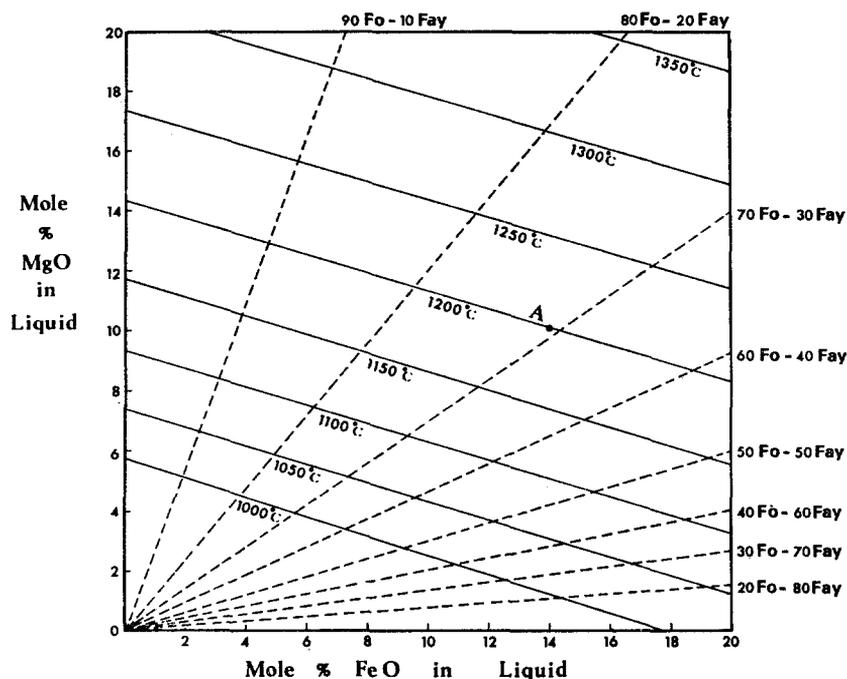


Fig. 7. Olivine saturation surface as determined by the mole % MgO and FeO in the liquid and the equations described in the text

to plot the surface in terms of the activity of $\text{MgSi}_{0.5}\text{O}_2$ against the activity of $\text{FeSi}_{0.5}\text{O}_2$ in the liquid. In order to use the diagram for actual basaltic liquids, it would then be necessary to determine the activity coefficients of the various species. Instead of doing this, we have used empirical equations calculated from experimental data on basalts. These empirical equations were used to extrapolate to the conditions shown on Fig. 7. The greater the deviation of the temperature and compositions from those used in the experiments, the greater the error in using Fig. 7.

A few examples will be given to demonstrate the usefulness and limitations of the liquidus projection. A liquid containing 10 mole per cent MgO and 14 mole per cent FeO (Point *A*) can coexist at equilibrium with olivine only at 1200° C. At temperatures greater than 1200° C a liquid of this composition cannot coexist at equilibrium with olivine, but it could coexist with some other phase such as plagioclase or chrome spinel. If olivine is the first phase to crystallize from a liquid of this composition, the liquidus temperature is 1200° C and the composition of the first olivine crystals is 70% forsterite—30% fayalite. If a phase containing no iron or magnesium, such as plagioclase, starts to crystallize at a temperature greater than 1200° C, this will increase the temperature at which olivine will crystallize, because both the mole per cent FeO and MgO in the liquid will be increased to a value greater than *A*. The early crystallization of plagioclase will not affect the composition of the first olivine (70 Fo—30 Fa) but will only increase the temperature of the first olivine crystallization. The temper-

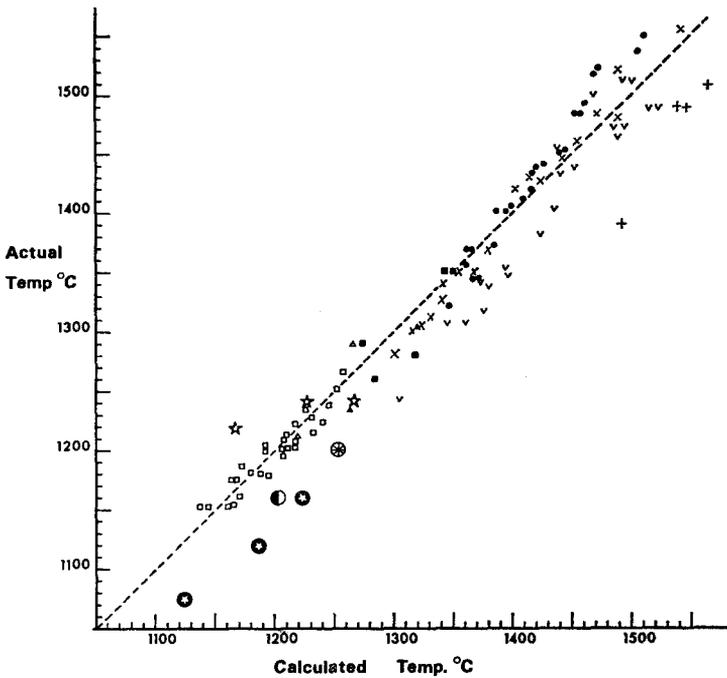


Fig. 8. The temperature calculated using the equations described in the text is compared to the actual temperature for a series of runs at the olivine liquidus. The data of the present study which are used to calculate the equations have also been shown (by open squares). The data are from the following sources: \blacktriangle Yoder and Tilley (Basalt experiments); \blacksquare Green and Ringwood (Basalt experiments 4.5 and 9.0 kb); \triangle Green T. (Basalt experiments 4.5 and 9.0 kb); \star Fudali R. (Basalt experiments); \star Hakli and Wright (Lava at Kilauea); \odot Moore and Evans (Prehistoric Makaopuhi Lava Lake, actual temperature assumed to be 1200° C); \bullet Peck, Wright and Moore (Alae Lava Lake, Hawaii); ∇ Bowen and Schairer (MgO-FeO-SiO₂); + Muan and Osborn (MgO-FeO-Fe₂O₃-SiO₂); \bullet Presnall (Forsterite-Diopside-Iron Oxide); \times Osborn and Tait (Forsterite-Diopside-Anorthite)

ature of a liquid of composition *A* can be lowered below 1200° C, but the liquid is then supersaturated with respect to an olivine of composition 70Fo-30Fa. Thus, if olivine is the first phase to crystallize, Fig. 7 can be used to predict the composition of olivine which will crystallize and the temperature of equilibrium crystallization, solely on the basis of the bulk chemical analysis of the whole rock.

The usefulness of Fig. 7 will depend upon how effectively it can predict olivine composition and the liquidus temperature for petrologically interesting compositions. In Fig. 8, we have plotted the observed (actual) temperature for the olivine saturation (liquidus) surface against the calculated temperature (same as from Fig. 7) for a number of silicate systems and for experiments on basalts. All the experimental data for the olivine primary phase volume have been plotted for the Mg-Fe-Si-O system (Bowen and Schairer, 1935; Muan and Osborn, 1956), a system with no iron (Mg₂SiO₄-CaMgSi₂O₆-CaAl₂Si₂O₈, by Osborn and Tait, 1952), a system run at various oxygen fugacities (Mg₂SiO₄-CaMgSi₂O₆-FeO-Fe₂O₃, Presnall, 1966), and for natural materials run at one atmosphere and higher pressures. We have also included all the experimental runs used in the present

study as a basis for the equations and the graph in Fig. 7. These runs were included in Fig. 8 in order to give an idea of the variability of these data and the range in temperature over which we have conducted experiments. The actual and calculated temperature are surprisingly close, considering the wide range in composition of samples and the temperature range over which the calculations have been extrapolated. For this reason, it is believed that the graph in Fig. 7 is a very useful first approximation of the olivine saturation surface, and can be used as a general guide to help in interpreting the thermal and chemical history of olivine crystallization.

The liquid composition of five samples from Hawaii for which the temperatures have been directly determined have been used to calculate a temperature and olivine composition. The calculated and actual olivine compositions are in close agreement (Fig. 6); however, the calculated temperature for all five is from 45 to 65° C too high (circles, Fig. 8). One possible explanation is that these liquids are supersaturated with respect to olivine, and thus the liquids contain more MgO and FeO that can coexist at equilibrium at the temperatures which have been measured.

In conclusion, the experimental results of the present study have been used to derive a number of empirical relationships between olivine and silicate liquids which can be used for better understanding of the early crystallization of basalt in nature. The temperatures, olivine compositions and the general configuration of the saturation surface shown on Fig. 7 all appear to be essentially correct. This illustrates that even in multicomponent, natural silicate systems, we can predict the relative changes in temperature of crystallization and composition of phases when the composition of the liquid is changed. These same general principles can be used for other mineral groups (pyroxene, plagioclase, spinel); however, the equations will be much more complicated and more attention will need to be paid to the formation of complexes in the silicate liquid.

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References

- Bowen, N. L., Schairer, J. F.: The system MgO-FeO-SiO₂. *Am. J. Sci.* **29**, 151-217 (1935).
Bradley, R. S.: Thermodynamic calculations on phase equilibria involving fused salts. Part II. Solid solutions and application to the olivines. *Am. J. Sci.* **260**, 550-554 (1962).
Brown, G. M.: The layered ultrabasic rocks of Rhum, Inner Hebrides. *Phil. Trans. Roy. Soc. Lond. Ser. B* **240**, 1-53 (1956).
Campbell, F. E., Roeder, P. L.: The stability of olivine and pyroxene in the Ni-Mg-Si-O system. *Am. Mineralogist* **53**, 257-268 (1968).
Darken, L. S., Gurry, R. W.: The system iron-oxygen I. The Wustite Field and related equilibria. *J. Amer. Chem. Soc.* **67**, 1398-1412 (1945).

- Emslie, R. F.: The Michikamau Anorthositic Intrusion, Labrador. *Can. J. Earth Sciences* **2**, 385–399 (1965).
- Fudali, R. F.: Oxygen fugacities of basaltic and andesitic magmas. *Geochim. Cosmochim. Acta* **29**, 1063–1075 (1965).
- Green, T. H., Ringwood, A. E.: The genesis of basaltic magmas. *Contr. Mineral. and Petrol.* **15**, 103–190 (1967).
- Hakli, T. A., Wright, T. L.: The fractionation of nickel between olivine and augite as a geothermometer. *Geochim. Cosmochim. Acta.* **31**, 877–884 (1967).
- Hill, R. E. T.: The crystallization of basaltic melts as a function of oxygen fugacity. Ph. D. Thesis, Queen's University (1968).
- Roeder, P. L.: Stability of spinel in basaltic melts. *Geol. Soc. Am. Annual Meeting Abstract*, 96–97 (1967).
- Irvine, T. N.: Chromian spinel as a petrogenic indicator. Part I, Theory. *Can. Jour. Earth Sci.* **2**, 648–672 (1966).
- Kennedy, G. C.: Equilibrium between volatiles and iron oxides in igneous rocks. *Am. J. Sci.* **246**, 529–549 (1948).
- Some aspects of the role of water in rock melts. *Geol. Soc. Am. Special Paper* **62**, 489–503 (1955).
- Medaris, L. G., Jr.: Partitioning of Fe⁺⁺ and Mg⁺⁺ between coexisting synthetic olivine and orthopyroxene. *Am. J. Sci.* **267**, 945–968 (1969).
- Morse, S. A.: The geology of the Kiglapait layered intrusion, coast of Labrador, Canada. Unpub. Ph. D. thesis, McGill Univ. (1961).
- Muan, A., Osborn, E. F.: Phase equilibria at liquidus temperatures in the System MgO–FeO–Fe₃O₃–SiO₂. *Am. Ceramic Soc. J.* **39**, 121–140 (1956).
- Nafziger, R. H., Muan, A.: Equilibrium phase compositions and thermodynamic properties of olivines and pyroxenes in the system MgO–“FeO”–SiO₂. *Am. Mineralogist* **52**, 1364–1385 (1967).
- Osborn, E. F., Tait, D. B.: The system Diopside-Forsterite-Anorthite. *Am. J. Sci. Bowen Volume*: 413–433 (1952).
- Peck, D. L., Wright, T. L., Moore, J. G.: Crystallization of tholeiitic basalt in Alae Lava Lake, Hawaii. *Bull. Volcanol.* **29**, 629–655 (1966).
- Presnall, D. C.: The Join Forsterite-Diopside-Iron oxide and its bearing on the crystallization of basaltic and ultramafic magmas. *Am. J. Sci.* **264**, 753–809 (1966).
- Roeder, P. L., Emslie, R. F.: Olivine—liquid equilibrium in basaltic melts. *Geol. Soc. Am. Annual Meeting Abstract*, 251 (1968).
- Smith, C. H., Kapp, H. E.: The Muskox Intrusion, a recently discovered layered intrusion in the Coppermine River area, Northwest Territories, Canada. *Min. Soc. Amer. Special Paper* **1**, 30–35 (1963).
- Smith, J. V.: X-ray-emission microanalysis of rock-forming minerals I. Experimental techniques. *J. Geol.* **73**, 830–864 (1966).
- Wager, L. R.: The major element variation of the layered series of the Skaergaard intrusion and a reestimation of the average composition of the hidden layered series and of the successive residual magmas. *J. Petrol.* **1**, 364–398 (1960).
- Brown, G. M.: Layered igneous rocks, 588 p. Edinburgh: Oliver and Boyd Ltd. 1967.
- Deer, W. A.: Geological investigations in East Greenland, Pt. III. The petrology of the Skaergaard Intrusion, Kangerdlugssuag, East Greenland. *Medd. Groenland* **105**, No 4, 1–352 (1939).
- Williams, R. J., Eugster, H. P.: An experimental study of (Fe, Mg) olivine—(Fe, Mg) pyroxene reactions and their geological applications. *Geol. Soc. Am. Annual Meeting Abstract*, 237 (1969).
- Yoder, H. S., Jr., Tilley, C. E.: Origin of basalt magmas: An experimental study of natural and synthetic rock systems. *J. Petrol.* **3**, 342–532 (1962).

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