

*Chemical analysis of olivines by the  
electron microprobe*

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*Summary.* Thirty-one natural olivines, of which 25 had been previously analysed by wet chemical methods, have been analysed for Mg, Fe, Mn, Ca, Ni, and Co by electron-microprobe techniques. The totals of the olivine molecules Fo, Fa, etc., calculated from the above metals vary from 97.6 to 101.5 with a mean of 99.6 %. Twenty-one of the specimens had been used previously by Yoder and Sahama to prepare a determinative curve between mole per cent. Fo and the lattice spacing  $d_{130}$ . Yoder and Sahama had found that the data for natural olivines showed large random displacements from a straight line, and that the best straight line deviated for low Fo values from that for synthetic olivines. A plot of Fo determined from the microprobe vs.  $d_{130}$  corrected for lattice expansion caused by Ca and Mn shows no systematic deviation between natural and synthetic specimens, and only small deviations from the best continuous curve (maximum 4 % in Fo assuming no error in  $d_{130}$ ). The maximum contents found for Mn, Ca, Ni, and Co were 3.2, 0.54, 0.33, and 0.03 %, respectively. For these minor constituents, some of the wet chemical analyses agreed very well with the microprobe results while others showed large deviations. Although the substitution of Ca is small, it can affect considerably the determination of mole per cent. Fo from  $d_{130}$ .

After specimen preparation and calibration have been carried out, microprobe analyses for most major and minor (but not trace) elements in common silicates can be made with an accuracy of about 0.5 to 5 % of the amount present in about one minute for each group of three elements. Although standard chemical methods applied to large homogeneous samples will retain their fundamental reference value, microprobe techniques with their high spatial resolution, relative freedom from contamination problems, high speed, and moderate to good accuracy promise to revolutionize analytical programmes in mineralogy and petrology.

THE scientific investigations of Professor C. E. Tilley have been characterized by their quantitative basis, especially in the systematic use of careful analyses prepared by a series of chemical analysts. This aspect is clearly demonstrated in his recent researches on mineral assemblages in alkaline rocks and on the mineralogy and petrology of basalts; indeed, his use of chemical analyses has intensified in recent years. Consequently, we feel it appropriate to offer this paper for inclusion in the volume honouring the scientific achievements of Professor Tilley. From his eagerness in taking advantage of the wide opportunities

of this new technique of microanalysis, it is certain that we may expect many more years of questing endeavour from this distinguished scientist.

Fortunately, the appearance of a new text on electron-probe microanalysis (Birks, 1963) makes it unnecessary to describe in detail the basic theory of the analytical technique. Briefly, an electron beam is focused on to the sample, and emitted X-rays are analysed for wavelength and intensity to give the type and concentration of elements present in the sample. Currently the range of elements that can be studied in commercial microanalysers is from Na to U. The electron microprobe was initially devised for fine-scale analysis, for the electron beam can be focused on to a spot of diameter less than  $10^{-4}$  cm, and the electrons need penetrate only 1 to  $2 \times 10^{-4}$  cm if the accelerating voltage is low enough. However, we feel that the instrument has equally great value for the analysis of coarse mineral grains because of the speed and ease of analysis. Although we see no evidence at this time for the supplanting of standard wet chemical methods for providing very accurate absolute analyses of large homogeneous samples, we think that for routine analysis of major elements in minerals the electron microprobe may become the most used analytical instrument for the following reasons: with the microprobe, tedious separation is unnecessary, spatial variation is easily determined, and analyses are rapid; other rapid methods based on refractive indices and lattice spacings are often seriously affected by minor constituents. We are developing analytical techniques for the major mineral groups with the aim of making possible a rapid analysis of all the minerals in common rocks. This paper uses some results on the olivine group to illustrate the potentiality of the microprobe analytical technique.

Because electron-probe microanalysis gives only relative results, it is necessary to develop a set of reference standards, preferably as close in composition as possible to the samples to be analysed. Olivines have proved to be extremely suitable for pioneer studies because of the generous donation via Dr. H. S. Yoder, Jr., and Dr. C. H. Smith of a suite of synthetic Mg-Fe olivines prepared by Dr. N. F. H. Bright of the Geological Survey of Canada and a synthetic tephroite from Dr. R. B. Snow of the U.S. Steel Company (Snow, 1943). In addition, synthetic diopside donated by Dr. J. R. Goldsmith has proved to be a suitable standard for Ca. Dr. W. C. Phinney has generously supplied portions of four olivines analysed at the Minnesota Rock Analysis Laboratory. Dr. H. S. Yoder, Jr., has kindly supplied samples of most of the 31 analysed natural olivines collected from various sources in order to

relate  $d_{130}$  to the composition (Yoder and Sahama, 1957). We are indebted to Prof. L. R. Wager and Drs. G. W. DeVore, H. M. Gehman, M. H. Hey, K. Hytönen, R. Johnston, I. D. Muir, C. S. Ross, and G. Switzer for permission to use these samples. Finally, Dr. I. D. Muir kindly supplied four olivines described by Tilley (1952) and Muir and Tilley (1961), Dr. Yoder a fayalite from a blast furnace and Dr. A. Turkevich a natural olivine; these have provided useful tests of the analytical techniques.

Olivines have proved to be especially suitable for pioneer studies because they approximate to a binary system, and the cell dimensions provide a test of the chemical composition. Yoder and Sahama (1957) were the first to use the spacing  $d_{130}$  as a measure of the Fo content of olivine, and others (Sahama and Hytönen, 1958; Jackson, 1960; Jambor and Smith, 1962) have developed the determinative technique in various ways. We shall use the observed values of  $d_{130}$  obtained by Yoder and Sahama, and our own measurements for eight specimens, to test the microprobe analyses of olivines.

#### *Microprobe techniques*

Samples were prepared by embedding mineral grains in epoxy cement filling in holes in brass disks. They were polished by rotating laps using, in order, 6 micron alumina powder, 8 micron, 1 micron, and  $\frac{1}{4}$  micron diamond pastes. The samples were sputtered with a layer of carbon to make them conducting.

The A.R.L. microprobe permits three elements to be analysed simultaneously. In the first run the conditions were:  $\text{CaK}_\alpha$ , 4 in. radius LiF spectrometer, flow proportional counter with Be window using P10 gas;  $\text{MgK}_\alpha$ , 4 in. mica spectrometer, 'Exatron' sealed gas proportional counter using Ne gas and Al window;  $\text{FeK}_\alpha$  (second order), 4 in. ADP spectrometer, 'Exatron' counter using A gas and Be window. In a subsequent run  $\text{MnK}_\alpha$  was run on the LiF spectrometer,  $\text{AlK}_\alpha$  on the mica spectrometer, and  $\text{TiK}_\alpha$  on the ADP spectrometer. Later  $\text{NiK}_\alpha$  and  $\text{CoK}_\alpha$  were run on the LiF spectrometer but using an 'Exatron' counter containing A gas, while  $\text{SiK}_\alpha$  was run on the ADP spectrometer. After careful alignment of a spectrometer all specimens were analysed for the appropriate element before changing to a new setting. Thus, the five spots measured for Fe, Mg, and Ca do not correspond to the spots for the other elements. Fe was run on the second order so that the data would be collected from a relatively stable sealed gas counter, while the small amount of Ca made it possible to use the

relatively unstable flow gas counter without significant error. [Since then, installation of a third 'Exatron' counter has permitted a switch of elements so that  $\text{FeK}_\alpha$  on the LiF spectrometer and  $\text{CaK}_\alpha$  on the ADP spectrometer are more desirable. In addition, the mica analysing crystal has been replaced by a KAP (potassium acid phthalate) crystal.]

In the recording console the specimen current and the outputs from the three counters may be used to charge four condensers. The analysis time can be controlled by terminating the analysis simultaneously on all four condensers when the first condenser reaches a set voltage. Then the voltages on all the condensers are printed on a potentiometric recorder. This system works well for conducting specimens because it compensates for variation of beam current with time. However, for non-conducting specimens it was not possible to control the conducting carbon layer sufficiently well to give a constant ratio between the beam current and specimen current for a given chemical composition, though usually the ratio was maintained within two per cent. Consequently, the present analyses were made on the basis of fixed time, which eliminates the problem of variable specimen conduction so long as there is no significant charging of the specimen. However, there was a drift of beam current which made necessary hourly calibration with the reference standards.

For high resolution a low accelerating voltage is required, but for analysis of large grains a higher voltage gives a greater yield of X-rays. Consequently, 25 kV was used in the analyses, together with a specimen current of about  $0.4 \mu\text{A}$ . Under these conditions sufficiently large numbers of quanta were generated in 20 seconds to yield a small enough statistical error.

The synthetic Mg-Fe olivines were used as reference standards for Mg and Fe. For Mn, synthetic tephroite on one-tenth beam current was used for calibration, together with a linear interpolation between the readings for forsterite and fayalite glasses for a zero reading. For Ca, Ni, Co, and Ti similar calibrations were made with diopside, nickel, cobalt, and titanium. Zero tests were also made by changing the wavelengths of the spectrometers to check for presence of Ca, etc., in the reference standards. (Actually, by wavelength scanning, about 0.01 % Ca was found in the synthetic Mg-Fe olivines and about 0.15 % Ca in the synthetic tephroite. Corrections were made for these amounts.) By reducing the beam current to one-tenth for the standards it was possible to stay in the linear range of the proportional gas counters. Duplicate analyses were made on each spot, and five spots, on different grains

when sufficient were available, were chosen for each specimen. The beam diameter was about 5 microns.

The following sources of error were considered: (a) wavelength overlap—no serious overlaps occur, though the  $\text{Co}K_\alpha$  line is affected by the  $\text{Fe}K_\beta$  line; (b) beam current variation—a non-linear drift (maximum 2% during eight hours) occurred during the analyses and it was corrected within an accuracy of 0.5%; (c) counter drift—the flow counter might have a non-linear rapidly-changing drift of up to 4% during a day while the 'Exatron' sealed counters are probably stable to 0.2%—the counter voltages and recorder sensitivities might drift by unknown amounts, but these changes would be taken care of by the hourly calibrations; (d) variation in the sputtered carbon layer would change the effective accelerating voltage and the absorption—the magnitude of this is unknown but is thought to be trivial because runs made with different coatings have given consistent results when fixed time analyses were used; (e) irregularity in the surface can change the absorption of the X-rays—because of the high take-off angle ( $52^\circ$ ) this is important only for the weak  $\text{Mg}K$  radiation: estimation is difficult because of possible chemical variation, but consistency of results from nearby spots of the same grain, and some theoretical arguments, suggest a possible error of the order of 1–2% for the state of polish of the present specimens—use of a wide beam reduces this effect by averaging—0.25 micron diamond probably gives surface irregularities less than 0.05 microns; (f) uncertainty in the reference standards—examination of the results for Mg and Fe shows that there is chemical variation in some of the synthetic Mg–Fe olivines; contrast the uniformity of  $\text{Fo}_{40}$  with variation for  $\text{Fo}_{55}$ , for example—for the minor constituents, the analytical uncertainty depends critically on the reference zero—by using wavelength scans to test the standards the uncertainty was reduced to 0.01% or less for Ca, Mn, Ni, and Co—calibration by standards like diopside which differ greatly in metal content involves both errors in the calibration of absorption and fluorescence factors and in possible non-linearity of the counters and records—it is thought that the error is within 5% of the amount present and more likely below 2%; (g) positioning of the specimen of the focusing circle of the spectrometer—very accurate focusing of the specimen on to the monochromator circle is necessary—tests suggest a possible random error of about 0.3% for any one measurement—the exact centre can be found by plotting counter output vs. position of specimen but the extra time involved rules out this procedure; (h) presence of impurities—each spot was carefully selected

in the microscope—if a very aberrant result was obtained, it was rejected; (i) sample variation—some specimens are seriously inhomogeneous and the mean of analyses taken at just five spots cannot give a good approximation to the average composition—movement of the specimen during the analysis would give a better estimate of the bulk composition, but would also increase the chance of including an impurity in the analysis; (j) change of composition in the analysed volume—some materials such as alkali feldspars and carbonates are so prone to damage by the electron beam (probably a combination of heating and electrical action) that it is difficult to obtain an analysis of a small volume—olivines are highly refractory; however, the use of a very high beam current ( $0.4 \mu\text{A}$ ) focused on to a small spot of diameter about 5 microns may have led to some specimen damage because the second of the two analyses on each point is, on average, about 0.4 % lower for  $\text{FeK}_\alpha$  radiation and 0.8 % lower for  $\text{MgK}_\alpha$ —it is possible, however, that the olivines are actually undamaged and that the reduction of X-rays during the second analysis is caused by a contamination deposit formed by breakdown of diffusion pump oil—it can be shown that a thickness of carbon about  $500 \text{ \AA}$  thick will absorb 1 % of the emerging  $\text{MgK}_\alpha$  radiation and 0.01 % of the  $\text{FeK}_\alpha$  radiation—in addition, the effective accelerating voltage of the electrons is reduced by the carbon film—the larger fall for the Mg readings would be consistent with this explanation—the effect on the analyses of the change in the surface composition of the olivine and carbon film is trivial because the reference standards and the analysed specimens can be expected to be affected similarly; (k) statistical error of the X-ray quanta—because individual quanta were not counted, this is hard to judge in view of the systematic difference between the duplicate readings: however, the data in table I, after correction for the effect described in (j), suggest a standard deviation near 0.2 % for Mg and 0.4 % for Fe—because duplicate readings on five spots were made, the error of the mean from this cause is almost certainly smaller than the sum of the other errors.

Fig. 1 is a plot of the probe value of Mg vs. the probe value of Fe for all the specimens. The averaged data for the synthetic specimens, with the exception of  $\text{Fo}_{55}$ , lie closely on a curve, but there is an irregularity of position along the curve amounting to about one division. That the points lie closely to a curve shows that there is a close negative correlation between the Mg and Fe readings. Changes of beam current and recorder sensitivity would lead to a positive correlation. Absorption errors for Mg would give a zero correlation. That the points for the

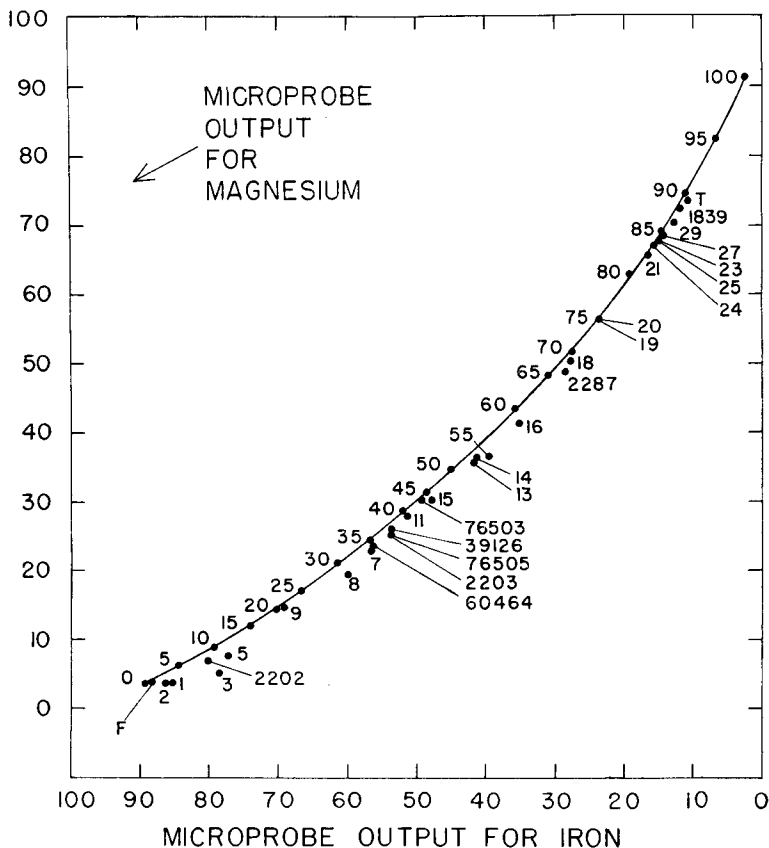


FIG. 1. Relation between microprobe outputs for Mg and Fe for all the olivines used in the present study. Each point is the mean of five sets of duplicate analyses, except for  $Fo_0$  and  $Fo_{100}$  glasses for which many more analyses were made. The data are given in tables I and II. The numbers above the curve refer to weight per cent. of the  $Fo$  molecule in the synthetic samples, and the curve has been drawn visually to give a good fit to these data. F refers to a blast furnace fayalite supplied by Dr. H. S. Yoder and T to a natural olivine supplied by Dr. A. Turkevich. The specimens labelled 1 to 29 refer to the samples listed in Yoder and Sahama's paper; 1839, 2202, 2203, and 2287 are from the Minnesota Rock Analysis Laboratory; 39126 is described by Tilley (1952), and 60464, 76503, and 76505 by Muir and Tilley (1961).

In evaluating the diagram it should be noted that the scale for Fe has been reversed so that points falling below the line may indicate substitution of (Mg,Fe) by other elements. Errors in correction for the beam current variation would displace points perpendicularly to the curve: the closeness of the points for synthetic olivines to the curve indicates that the beam current correction has been applied successfully. Irregularity of spacing along the curve of the data for the synthetic samples suggests differences between the mean composition of the analysed spots and the bulk composition.

synthetic olivines are irregularly spaced shows that there is some composition variation, and implies that the mean of analyses for five spots does not give an exact determination of the bulk composition. For some specimens, the spread of the analyses is quite large (table I). Most of the natural specimens fall below the curve and none lie above it in conformity with the expected presence of substituents like Mn and Ca. Although no rigorous deduction can be made, the reasonableness of the data gives confidence that the experimental errors of the means of the ten observations in the determination of Mg and Fe are in the range of 0.5 to 2 %, and encourage a detailed evaluation of the results.

#### *Calculation of results*

Table I shows the potentiometer readings for Mg and Fe obtained for the synthetic Mg-Fe olivines. Duplicate readings for five spots and the overall mean value are listed. The mean and range are plotted in figs. 2 and 3 against the weight per cent. of Mg and Fe calculated from the listed composition. The irregularity of points is the result both of error in the probe readings and of an insufficient approximation of the mean of five analyses to the listed bulk composition. In order to use these data as a calibration for the natural olivines a polynomial was fitted by least squares techniques to each set of data, assuming no error in the listed composition. Because the error in the probe readings is approximately proportional to the amount of the element, except for small values where the error tends to an absolute value, the uncertainty of the calibration will increase with the element concentration. Because only five spots were analysed for each sample, the composition range of each sample is only approximately known. Thus, there is only a qualitative basis on which to decide whether to apply a weighting scheme to the data. An unweighted third-order polynomial (omitting the deviant  $\text{Fo}_{55}$  specimen) gave a satisfactory fit between the probe and chemical values of Fe for the synthetic olivine, and the random distribution of residuals with composition made it unnecessary and undesirable to go to a higher order. Difficulty was encountered in calculating a suitable polynomial for the Mg data. A third-order polynomial calculated on the basis of equal weights for each composition, except for the arbitrary omission of the data for  $\text{Fo}_{55}$ , did not lead to a random distribution of residuals with composition (table I and fig. 2). For both ends there was a systematic deviation. The effect of weighting the data to take account of the greater spread of readings for the larger Mg-values was tried, but the systematic deviation remained. Consequently, a



TABLE I. Analyses of Fe-Fe glasses

Composition (wt. % Fe)	Mg analyses					Fe analyses					Calculated value				
	Calculated values					Calculated values									
	1	2	3	4	5	Mean	1	2	3	4		5	Mean		
100	70 values obtained during calibration					91.1	90.3	90.3	70 values	6.8	6.8	7.2	6.9	2.8	2.71
95	83.3	82.9	83.2	82.6	81.9	82.4	82.5	82.5	6.8	6.7	7.0	7.2	6.9	6.9	6.80
90	82.7	82.0	82.6	81.8	81.1	74.7	75.2	75.6	11.3	11.2	10.9	11.0	11.1	11.1	11.01
85	74.7	73.3	76.0	73.7	74.7	69.2	68.7	69.2	11.3	11.1	10.7	10.9	11.0	11.1	11.01
	69.2	69.0	69.0	70.1	70.2	69.2	68.7	69.2	14.2	14.3	14.2	15.0	15.1	14.6	15.05
	68.3	68.4	68.4	69.6	70.0	63.0	62.4	62.9	14.2	15.3	14.2	14.9	14.8	19.1	19.24
80	62.8	62.8	62.6	63.2	65.0	63.0	62.4	62.9	19.2	18.9	19.2	19.2	19.0	19.1	19.24
	61.6	62.8	61.7	63.2	64.4	56.5	57.0	57.4	19.1	18.8	19.1	19.3	19.0	23.6	23.27
75	57.8	56.5	55.5	55.8	57.5	56.5	57.0	57.4	22.8	23.8	23.8	23.5	23.7	23.6	23.27
	56.9	57.0	55.2	55.5	57.3	51.4	52.1	52.2	27.8	26.5	28.2	28.3	26.7	27.5	27.30
70	52.6	52.7	50.6	49.3	51.9	48.5	47.6	47.5	27.1	26.7	28.3	28.4	26.6	31.49	27.30
	52.2	52.9	50.2	49.3	52.3	48.5	47.6	47.5	31.6	29.8	29.6	33.1	30.0	30.8	31.49
65	47.6	49.6	49.7	46.5	49.5	43.6	43.1	42.8	34.9	36.5	34.6	36.4	35.1	35.4	35.56
	47.6	49.6	49.7	46.5	49.5	43.6	43.1	42.8	34.9	36.5	34.6	36.4	35.1	35.4	35.56
60	43.6	42.1	44.1	42.9	45.4	36.6	n.c.	n.c.	37.8	38.6	39.8	39.8	40.0	39.1	n.c.
	43.6	42.1	44.1	42.9	45.4	36.6	n.c.	n.c.	37.8	38.6	39.8	39.8	40.0	39.1	n.c.
55	35.1	30.9	39.3	39.8	37.9	34.6	35.3	34.9	38.0	38.8	39.3	39.5	39.7	44.8	43.92
	35.2	30.5	39.2	39.8	37.9	34.6	35.3	34.9	38.0	38.8	39.3	39.5	39.7	44.8	43.92
50	32.1	35.1	34.7	35.0	36.7	31.4	31.6	31.3	47.3	44.0	44.2	43.9	44.1	48.5	48.08
	32.0	35.3	34.2	34.5	36.8	31.4	31.6	31.3	47.3	44.0	44.2	43.9	44.1	48.5	48.08
45	31.0	31.6	31.3	31.6	31.9	28.9	27.9	27.6	48.3	48.6	48.6	47.8	48.0	51.9	52.45
	31.0	31.5	31.2	31.1	31.6	28.9	27.9	27.6	48.3	48.6	48.6	47.8	48.0	51.9	52.45
40	29.8	28.9	28.1	29.2	28.8	28.9	27.9	27.6	52.0	51.9	52.0	51.8	51.9	51.9	52.45
	29.7	28.7	28.1	29.1	28.9	28.9	27.9	27.6	52.0	51.9	52.0	51.8	51.9	51.9	52.45

TABLE I. (*Cont.*)

Composition (wt. % Fe)	Mg analyses					Fe analyses								
	1	2	3	4	5	Mean	1	2	3	4	5	Mean	Calculated value	
35	24.9	22.9	24.9	24.1	25.7	24.4	24.5	24.4	57.0	58.3	56.6	56.9	55.2	56.7
	24.8	22.7	24.7	23.8	25.7				57.0	57.6	56.2	56.6	55.6	
30	21.1	21.7	20.2	21.5	22.2	21.3	21.2	21.3	61.6	61.0	62.0	60.7	61.0	61.20
	21.0	21.7	20.5	21.2	22.3				61.2	61.1	61.6	60.2	60.6	
25	17.2	17.2	17.1	17.1	17.2	17.2	17.8	18.1	63.9	66.2	68.0	67.0	66.6	65.60
	17.3	17.5	17.0	17.1	17.2				64.9	66.8	66.5	66.5	66.8	
20	14.3	13.1	15.6	15.8	14.6	14.7	14.8	15.2	70.8	70.8	69.6	69.2	70.6	70.07
	14.2	13.1	15.6	15.8	14.6				70.5	69.9	69.5	69.2	70.0	
15	12.2	11.7	12.0	12.0	12.7	12.1	11.8	12.2	74.0	74.9	74.1	74.9	72.9	74.80
	12.0	12.0	11.8	12.0	12.4				74.0	74.1	73.7	74.0	72.5	
10	9.1	9.1	9.1	8.9	8.9	9.0	9.0	9.4	79.8	80.1	79.1	78.3	79.8	79.45
	9.0	9.1	9.3	8.8	8.8				79.6	79.6	79.6	78.4	79.3	
5	6.5	6.4	6.3	6.6	6.8	6.5	6.3	6.3	84.9	84.5	84.9	85.0	84.7	84.37
	6.5	6.7	6.2	6.7	6.5				84.5	84.6	85.0	84.4	83.9	
0	80 values obtained during calibration					3.8	3.96	3.3	80 values				89.4	89.22

The vertical pairs of numbers are duplicate analyses.

The first column of calculated Mg readings were obtained from a fourth-order polynomial using the following terms in ascending order: 3.962, 1.289, 0.05205, -0.002061, -0.0000457. The second column is for a third-order polynomial using the terms 3.304, 1.7786, -0.015982 and 0.001077. The calculated Fe readings were obtained from a third-order polynomial using the terms 2.7078, 1.5195, -0.002206 and 0.000060.

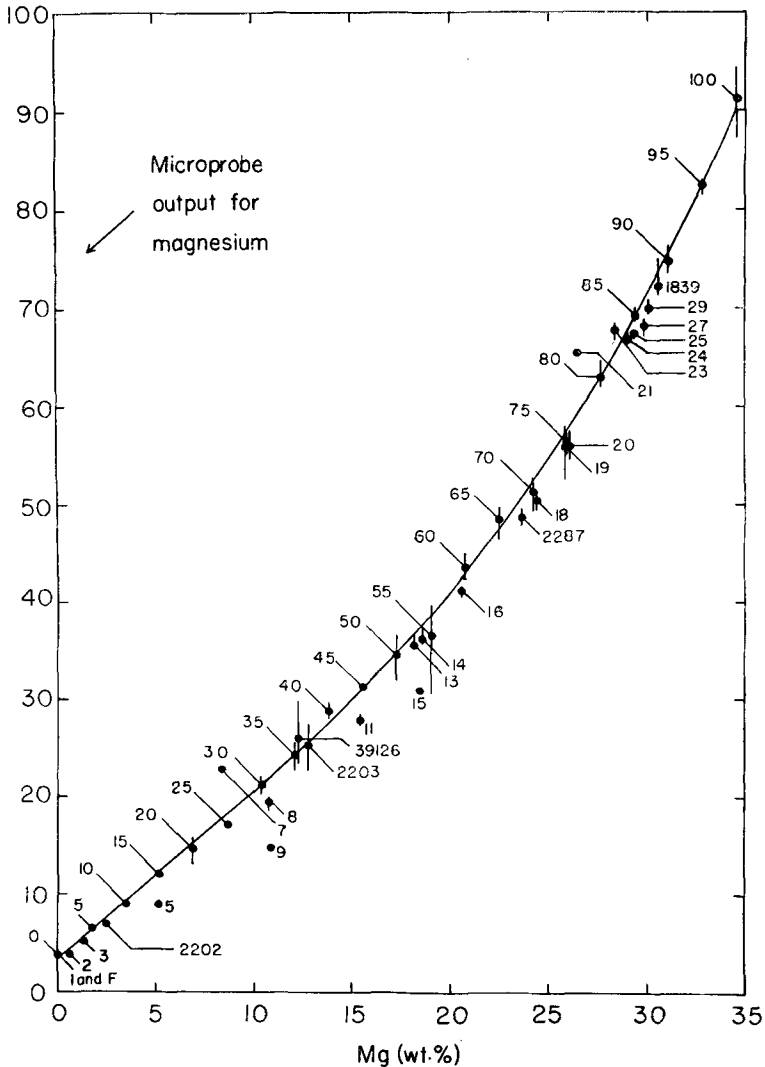


FIG. 2. Microprobe output for Mg in arbitrary units vs. the prepared weight per cent. of Mg for the synthetic samples or the analysed weight per cent. Mg calculated from MgO reported by the chemical analyst. The mean and spread of the five sets of duplicate measurements for each specimen are shown by the filled circle and the line. The curve is the third-order polynomial fitted by least squares method to all the synthetic data, equally weighted except for the omission of the data for  $Fe_{0.55}$ . The very large range for  $Fe_{0.100}$  is caused merely by two analyses out of seventy, and most of the values are within one unit of the mean. See legend to fig. 1 for the labelling of the specimens.

fourth-order polynomial was calculated using the same weighting scheme. The residuals were now randomly distributed, and the only unsatisfactory feature was the deviation of  $-0.11$  between the observed and calculated values for  $F_{0_0}$  which leads to small negative values for Mg

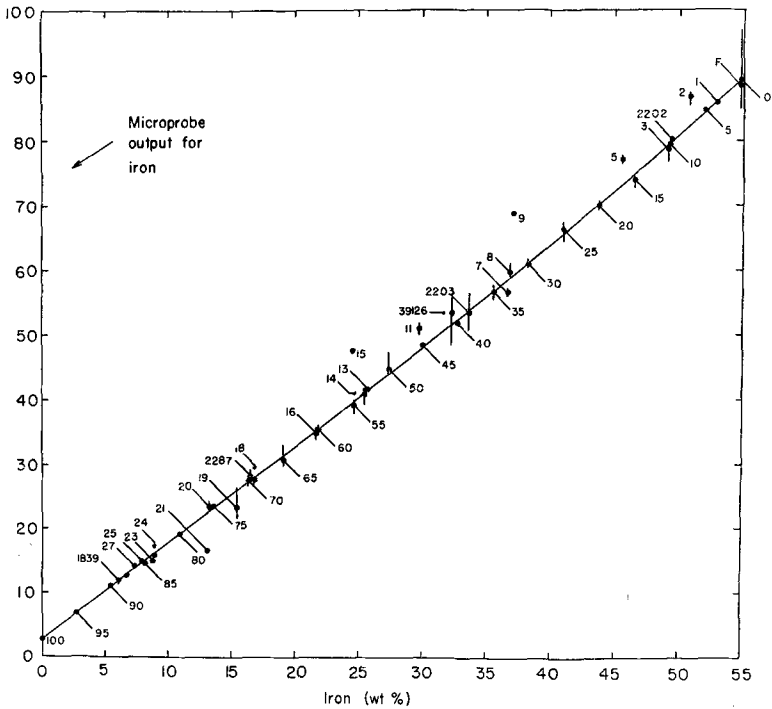


FIG. 3. Microprobe output for Fe vs. weight per cent. Fe. The data for  $F_{0_{55}}$  were omitted when the third-order polynomial was calculated. The very large range for  $F_{a_{100}}$  is caused merely by two analyses out of eighty, and nearly all values are within one unit of the mean. See legend to fig. 2 for further details.

of three of the natural olivines which are essentially Mg-free. The weights applied to the data ranged uniformly from 5 for  $F_{0_0}$  to 1 for  $F_{0_{95}}$ ;  $F_{0_{100}}$  was given weight 5 because it should be more homogeneous and because 70 calibration values were obtained. Increasing the weight of  $F_{0_0}$  would have led to a better fit at this composition: however, objection can be made to the practice of adjusting weights in an attempt to improve the calibration curve. Consequently, no further calculations

were made. It is not possible to give an accurate numerical estimate of the error of the calibration because a systematic error may result from the compositional variation. The largest residuals, except for  $Fe_{0.55}$ , between the calculated and observed values are 1.0 for Mg and 0.9 arbitrary units for Fe. Fitting the polynomials will have reduced the uncertainty in the calibration below this figure. It is suggested that for low values the uncertainty is about 0.1 to 0.2 arbitrary units, while for high values the uncertainty becomes proportional to the amount present—perhaps 0.5 to 1.0 %.

The Mg and Fe outputs for the natural samples are given in table II and plotted against the chemically-determined metal contents in figs. 2 and 3. Table III shows the weight per cent. of Mg and of Fe determined from the calibration curves established for the synthetic specimens. Table II also contains data for Ca and Mn which are shown graphically in fig. 4 (a) and (b) along with data for synthetic diopside and tephroite used as calibrants. These latter data were corrected for absorption. The probe analyses for Ca and Mn are listed in table III together with average analyses for Ni and Co for which details of individual analyses are not given in order to save space. Table III also contains the weight per cents. of the formula units forsterite, fayalite, tephroite, larnite, and  $Ni_2SiO_4 + Co_2SiO_4$  together with the summation. Also listed in the table are the molecular per cents. of the formula units totalled to 100 % together with the Fo values calculated from the wet chemical analyses. Measurements were also made for Si, Al, and Ti but are not included for the following reasons: the apparent Ti and Al contents are close to zero for all specimens, and lengthy analyses would be required to establish the actual compositions—the Si measurements were not accurate enough to contribute to any conclusions about the composition of olivines. It is planned to work on these elements later on.

The amounts of Mn, Ca, Ni, and Co are so small that it was not worth while to calculate the effect of absorption on the MgK and FeK radiation. The effect of matrix enhancement has also been neglected, because the enhancement of Mg by Si is taken care of by the calibration procedure and the enhancement of Ca by Fe is less than 1 % of the amount present on the average. As expected, the relation between Fe (probe) and Fe (chemical) is almost linear (of course, non-linearity of the counter and the recorder can affect the shape), while that between Mg (probe) and Mg (chemical) is strongly curved because of different absorption coefficients for  $MgK_{\alpha}$  in Mg-rich and Fe-rich matrices.

TABLE II. Microprobe readings for Mg, Fe, Ca, Mn

Specimen	Mg readings					Fe readings					Ca readings					Mn readings					
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	6
YS1	3.8	3.8	3.8	3.8	3.7	85.4	85.9	85.8	86.0	85.9	7.0	4.3	7.0	2.7	6.0	3.81	4.00	3.86	3.79		
YS2	3.8	3.8	3.9	3.9	3.9	87.4	86.8	85.3	87.1	86.7	6.6	20.2	39.5	8.4	9.6	1.54	1.47	1.80			
YS3	5.2	5.1	5.2	5.0	5.2	78.3	79.6	79.7	78.0	76.8	2.3	2.0	2.9	2.2	2.7	7.69	7.49	7.99			
YS5	8.8	8.7	8.6	9.5	8.7	77.5	76.9	77.7	76.8	76.4	8.1	8.7	10.0	8.3	21.0	1.32	1.32	0.38	0.79	1.95	1.91
YS7	22.9	23.2	23.0	22.9	22.5	57.2	56.3	56.4	56.1	57.3	2.0	1.9	1.9	1.8	2.3	3.26	3.12	3.19	3.21		
YS8	19.9	18.6	19.2	20.1	20.0	59.0	60.1	61.1	59.2	59.8	25.8	26.1	26.1	25.5	25.8	2.02	2.08	2.02			
YS9	14.9	14.8	15.0	14.5	14.8	68.8	69.2	68.8	69.0	68.7	6.7	5.0	6.1	7.0	5.7	1.41	1.41	1.47			
YS11	27.4	27.9	28.9	27.8	27.7	51.4	50.0	50.8	51.9	50.7	1.1	19.8	1.7	5.8	1.2	1.01	1.07	1.08			
YS13	35.4	35.2	36.9	35.3	35.3	41.6	41.8	40.3	42.5	42.2	17.3	17.3	16.8	15.4	17.2	1.14	1.14	1.20			
YS14	35.7	36.3	35.9	37.5	—	41.5	41.0	41.8	39.3	—	18.3	18.1	17.9	14.6	—	1.16	1.16	0.75	1.14		
YS15	29.9	29.9	30.2	30.4	30.2	48.1	48.0	47.5	47.2	47.6	5.7	5.4	6.3	6.9	6.0	0.96	0.92	0.94			
YS16	41.7	40.7	40.6	41.7	41.6	35.8	35.0	34.8	33.9	34.9	15.4	17.6	17.7	16.3	17.8	0.75	0.72	0.72			
YS18	51.7	50.1	50.3	50.8	49.4	27.7	28.1	27.7	26.5	27.8	12.0	11.8	14.6	13.3	12.9	0.55	0.55	0.60			
YS19	54.5	57.3	52.6	58.0	57.3	24.0	22.1	26.4	21.7	22.3	18.9	18.9	18.5	17.5	18.4	0.53	0.53	0.55			
YS20	54.6	56.1	55.2	56.8	57.5	24.3	23.5	24.1	22.8	23.0	16.3	17.0	16.6	20.6	18.0	0.52	0.56	0.55			
YS21	65.2	65.1	65.6	66.0	65.6	16.6	16.5	16.7	16.7	16.5	1.5	2.6	1.9	1.3	1.6	0.54	0.52	0.53			
YS23	66.8	68.3	68.2	67.4	68.5	15.5	15.0	14.7	15.3	14.6	19.6	18.6	19.6	20.0	16.8	0.38	0.41	0.47			
YS24	66.9	66.3	66.7	67.9	67.2	15.7	16.0	16.1	15.9	15.9	0.6	1.2	1.0	0.7	—	0.56	0.56	0.58			
YS25	67.5	67.6	67.7	66.8	67.7	15.0	15.1	15.1	14.9	14.9	1.9	2.6	2.0	2.5	1.7	0.30	0.27	0.26			
YS27	67.2	69.0	67.9	68.1	68.7	14.4	14.2	14.1	14.2	14.2	0.2	-0.3	0.0	0.0	0.2	0.26	0.26	0.26			
YS29	69.4	70.0	70.9	69.7	69.9	12.7	12.8	12.9	12.7	12.9	1.5	1.8	1.8	1.6	1.6	0.27	0.21	0.26			
R1839	71.3	71.8	71.6	75.1	71.9	12.4	12.3	12.2	11.3	11.8	-0.1	0.1	-0.2	-0.1	0.0	0.25	0.26	0.19			
R2202	7.0	7.0	7.0	7.0	7.1	79.8	79.4	80.3	80.6	80.6	12.7	16.7	17.9	16.7	16.5	2.11	2.16	2.17			
R2203	25.8	25.9	27.6	24.3	22.8	52.7	52.6	50.8	54.2	56.5	12.3	14.6	14.1	13.4	15.2	1.03	1.15	1.04	1.25	1.24	
R2287	47.9	49.1	49.2	49.6	47.9	29.3	27.4	28.6	27.8	27.9	2.4	2.8	3.4	3.1	3.0	0.54	0.54	0.49			
F	4.0	3.9	3.9	3.9	3.9	88.4	89.4	87.1	89.0	88.7	4.4	4.4	8.5	4.1	5.1	0.41	0.31	0.31	0.24		
T	71.5	74.0	74.7	71.8	74.9	10.7	10.9	11.0	10.8	11.0	0.1	0.4	0.1	-0.1	-0.1	0.23	0.23	0.21	0.22		
39126	29.9	24.1	23.6	23.5	29.3	48.5	56.4	56.3	56.6	50.3	18.6	22.7	21.7	24.3	20.5	1.66	1.54	1.31	1.56	1.48	
60464	24.8	24.8	21.4	23.8	—	54.5	54.5	59.5	56.3	—	16.7	13.7	15.9	12.8	13.4	1.31	1.47	1.44	1.72	1.87	
76503	29.2	28.3	32.4	31.0	30.0	50.4	50.4	50.4	48.6	48.9	22.7	23.1	15.1	16.8	17.1	1.49	1.81	1.86	2.15	2.47	
76505	26.0	24.5	25.1	25.2	26.8	53.5	55.0	54.4	54.0	50.5	30.8	30.7	29.0	30.3	39.1	2.14	2.09	1.74	1.88	2.12	

Each reading is the mean of duplicate analyses on the same position. Most pairs of analyses were made on separate grains; if insufficient grains were available, analyses were made on different places of the same grain. All readings are on an arbitrary scale. Those for Mg and Fe are not corrected for a zero reading, while those for Ca and Mn have been corrected (see text).

TABLE III. Microprobe analyses of olivines

Specimen	Microprobe values weight per cent. of metal								Microprobe values weight per cent. of formula unit							Chemical Fo %	Microprobe values mole per cent. totalled to 100						$d_{150}$ A	$d_{150}$ corrected A			
	Original	New	Mg	Fe	Mn	Ca	Ni	Co	Fo	Fa	Te	La	NC	$\Sigma$	Fo		Fa	Te	La	NC	Fo	Fa			Te	La	NC
USNM90468	YS1	(-0.11)	52.9	1.63	0.09	0.01	0.00	(-0.3)	96.5	3.0	0.2	0.0	(99.7)	2.6	(-0.5)	97.2	3.0	0.2	0.0	2.8310	2.8203						
EG4139	YS2	(-0.11)	53.4	0.70	0.28	0.00	0.00	(-0.3)	97.4	1.3	0.6	0.0	(99.3)	2.6	(-0.5)	98.5	1.3	0.7	0.0	2.8286	2.8286						
F	YS3	0.87	48.8	3.24	0.04	0.01	0.00	2.3	89.0	6.0	0.1	0.0	97.6	5.5	3.7	90.1	6.1	0.1	0.0	2.8310	2.8284						
EG4146	YS5	3.41	48.0	0.51	0.19	0.01	0.00	9.9	87.6	1.0	0.4	0.0	98.9	20.2	13.8	84.7	1.0	0.5	0.0	2.8213	2.8198						
USNM11913	YS7	11.28	35.6	1.34	0.03	0.01	0.00	32.6	64.9	2.5	0.1	0.0	100.1	32.3	41.2	56.6	2.2	0.1	0.0	2.8032	2.8021						
FEAE121	YS8	9.55	37.5	0.86	0.43	0.02	0.00	27.6	68.4	1.6	0.9	0.0	98.5	39.7	36.0	61.6	1.4	1.0	0.0	2.8077	2.8049						
EG1907	YS9	6.92	43.1	0.60	0.10	0.03	0.01	20.0	78.6	1.1	0.2	0.1	100.0	40.0	26.6	72.1	1.0	0.2	0.1	2.8126	2.8118						
E	YS11	13.80	32.0	0.44	0.10	0.04	0.01	39.9	58.3	0.8	0.2	0.1	99.3	53.9	49.3	49.7	0.7	0.2	0.1	2.7959	2.7952						
FEAE62	YS13	17.47	26.0	0.49	0.28	0.04	0.01	50.5	47.3	0.9	0.6	0.1	99.5	61.3	59.8	38.8	0.7	0.6	0.1	2.7920	2.7904						
FEAE66	YS14	17.77	25.4	0.44	0.29	0.04	0.02	51.4	46.3	0.8	0.6	0.1	99.2	62.2	60.8	37.8	0.7	0.6	0.1	2.7921	2.7905						
EG4077	YS15	14.87	29.9	0.40	0.10	0.09	0.01	43.0	54.5	0.7	0.2	0.2	98.6	63.1	52.8	46.2	0.6	0.2	0.2	2.7951	2.7945						
YS16	YS16	19.97	21.5	0.31	0.28	0.06	—	57.8	39.2	0.6	0.6	0.1	98.3	68.1	67.3	31.6	0.5	0.6	0.1	2.7882	2.7867						
E	FEAE74	YS18	23.61	16.6	0.24	0.22	0.15	0.02	68.3	30.3	0.4	0.5	0.3	99.8	76.4	75.8	23.2	0.3	0.4	0.2	2.7816	2.7806					
I	YS19	25.55	13.7	0.22	0.31	0.20	0.01	73.9	25.0	0.4	0.7	0.4	100.4	78.0	80.1	18.7	0.3	0.6	0.3	2.7799	2.7785						
FEAE139	YS20	25.55	13.9	0.23	0.30	0.10	0.02	73.9	25.4	0.4	0.7	0.2	100.6	80.6	80.0	19.0	0.3	0.6	0.2	2.7786	2.7772						
BMI192-9	YS21	28.51	9.3	0.22	0.03	0.04	0.00	82.5	17.0	0.4	0.1	0.1	100.1	80.8	87.2	12.4	0.3	0.1	0.1	2.7738	2.7735						
FEAE56	YS23	29.17	8.2	0.17	0.32	0.18	0.01	84.4	15.0	0.3	0.7	0.3	100.7	87.4	88.2	10.8	0.2	0.6	0.2	2.7746	2.7732						
YS24	YS24	28.93	8.8	0.24	0.01	0.04	0.00	83.7	16.1	0.4	0.0	0.1	100.3	87.4	88.0	11.7	0.3	0.0	0.1	2.7736	2.7735						
C	YS25	29.08	8.2	0.12	0.07	0.28	0.01	84.1	15.0	0.2	0.2	0.5	100.0	88.4	88.5	10.9	0.2	0.1	0.4	2.7728	2.7725						
B	YS27	29.28	7.6	0.11	0.00	0.33	0.01	84.7	13.9	0.2	0.0	0.6	99.4	89.9	89.3	10.1	0.2	0.0	0.4	2.7730	2.7729						
USNM53948	YS29	29.77	6.7	0.10	0.03	0.33	0.01	86.1	12.2	0.2	0.1	0.6	99.2	90.4	90.5	8.9	0.1	0.1	0.4	2.7718	2.7716						
R1839	YS30	30.37	6.1	0.09	0.00	0.27	0.01	87.9	11.1	0.2	0.0	0.1	99.3	91.8	91.8	8.0	0.1	0.0	0.1	2.7717	2.7717						
R2202	YS31	2.18	49.7	0.91	0.27	0.02	0.00	6.3	90.7	1.7	0.6	0.0	99.3	10.2	8.9	88.7	1.7	0.7	0.0	2.8257	2.8235						
R2203	YS32	12.50	33.5	0.48	0.20	0.05	0.01	36.2	61.1	0.9	0.4	0.1	98.7	45.5	45.5	53.2	0.8	0.4	0.1	2.8021	2.8009						
R2237	YS33	22.92	17.0	0.22	0.05	0.07	0.01	66.3	31.0	0.4	0.1	0.1	97.9	76.3	75.2	24.3	0.3	0.1	0.1	2.7817	2.7814						
F	(-0.04)	54.4	0.13	0.08	0.00	0.03	0.00	(-0.1)	99.2	0.3	0.2	0.0	(99.7)	—	(-0.2)	99.7	0.2	0.2	0.0	—	—						
T	YS36	5.4	0.08	0.00	0.26	0.01	0.00	88.7	9.9	0.1	0.0	0.5	99.2	—	92.5	7.1	0.1	0.0	0.3	—	—						
39126	YS37	12.90	33.6	0.60	0.36	0.05	0.01	37.3	61.3	1.1	0.8	0.1	100.6	44.7	45.9	52.2	1.0	0.8	0.1	2.8044	2.8022						
60464	YS38	11.68	35.3	0.60	0.24	0.05	0.01	38.8	64.4	1.1	0.5	0.1	99.9	—	42.4	56.0	1.0	0.5	0.1	2.8012	2.7997						
76503	YS39	14.92	30.8	0.78	0.34	0.02	0.00	43.2	56.2	1.4	0.7	0.0	101.5	—	51.7	46.4	1.2	0.7	0.0	2.7978	2.7958						
76505	YS40	12.60	33.6	0.78	0.34	0.03	0.00	36.5	61.3	1.4	1.2	0.1	100.5	—	45.1	52.4	1.2	1.2	0.1	2.8030	2.7999						

NC represents (Ni + Co)<sub>2</sub>SiO<sub>4</sub>. YS denotes specimens used by Yoder and Sahama.  $d_{150}$  corrected' is the result of applying the correction (0.0004 Te + 0.0022 La) to the observed  $d$  values. The first twenty-one  $d$ -values were measured by Yoder and Sahama and the last eight by us.

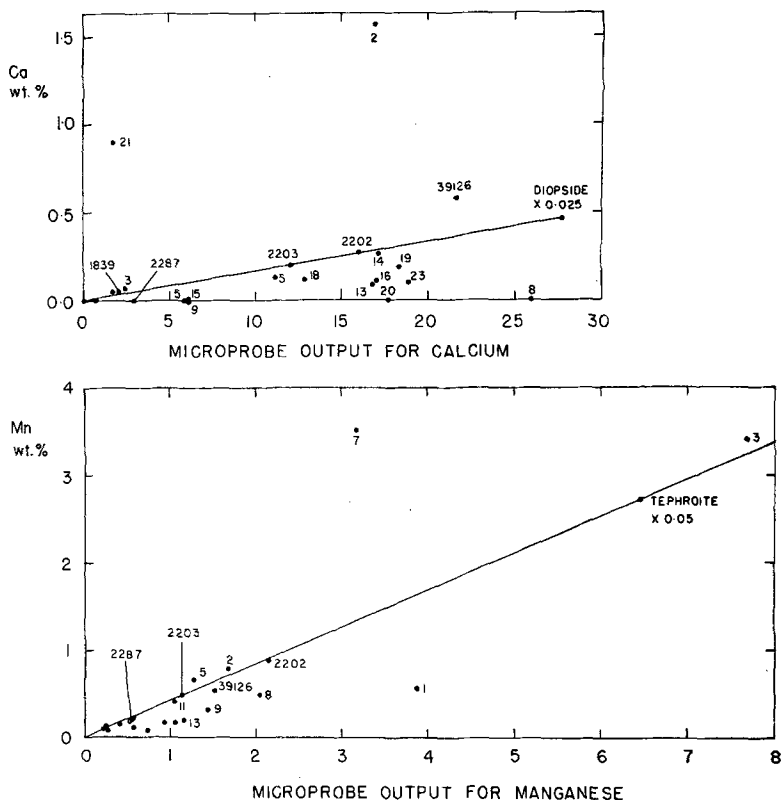


FIG. 4. Microprobe outputs for Ca and Mn vs. the weight per cents, calculated from CaO and MnO in the chemical analyses. The point for synthetic diopside, to which the straight line is drawn, has been moved to 1/40th of its true distance from the origin. Similarly the point for synthetic tephroite has been moved to 1/20th of its distance from the origin. Some of the points have been labelled with the specimen number.

#### *Significance of results*

The microprobe results can be tested in several ways: comparison of the cation sums with the theoretical formula; comparison with the measurements of the lattice spacing  $d_{130}$  made by Yoder and Sahama for 21 specimens and by us for another 8 specimens; and comparison with the wet chemical analyses.

Twenty-three of the 31 specimens give a summation of the formula units  $(Fo + Fa + Te + La + (Ni + Co)_2SiO_4)$  between 99 and 101, while all 31 lie within 2.4% of the ideal value of 100% (table III). Of course,



the presence of impurities might either increase or decrease the expected total; in addition, the presence of a coupled substitution such as  $\text{Fe}^{++} + \text{Si} \rightarrow 2\text{Fe}^{+++}$  would change the ideal value. However, the closeness of the results to 100 % is encouraging.

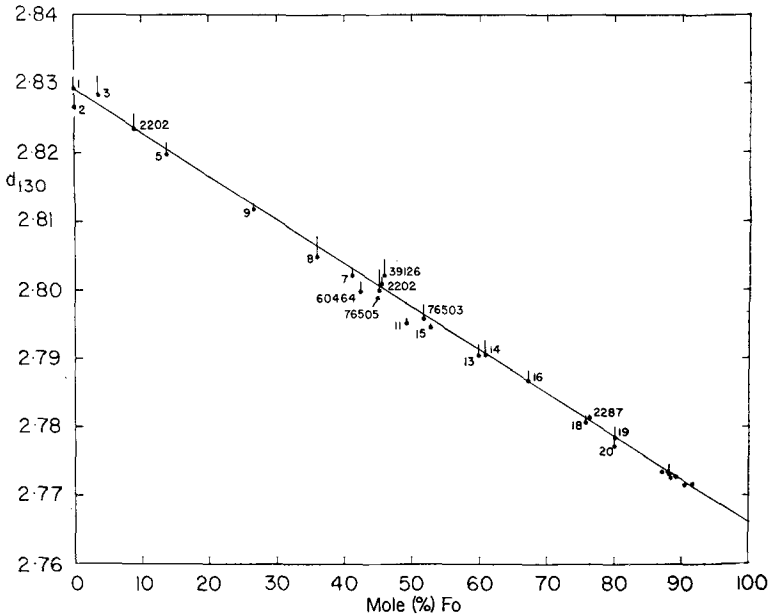


FIG. 5. Relation between  $d_{130}$  and microprobe value of mole per cent. Fo. The solid circle shows the value of  $d_{130}$  corrected for Ca and Mn substitution while the upper end shows the observed value of  $d_{130}$  (table III). The  $d_{130}$  values for 0 and 100 % Fo are the means of the several values quoted by Yoder and Sahama for synthetic samples. The straight line connecting the points for the synthetic samples lies above most of the corrected  $d$ -values for specimens of intermediate composition, and a curve passing through 50 % Fo and 2.7965 Å would fit the data better than a straight line.

The second test is complicated by the substitution of Ca, Mn, Ni, and Co for Mg and Fe. Fig. 5 shows a plot of  $d_{130}$  vs. the probe value for mole per cent. Fo (mole per cent. Fo =  $100\text{Mg}/(\text{Mg} + \text{Fe} + \text{Mn} + \text{Ca} + \text{Ni} + \text{Co})$ ). A correction to  $d_{130}$  was based on the cell dimensions and atomic radii as follows. Ni and Co were neglected because the contents are so small and the ionic radii lie between those for Mg and Fe. The cell dimensions of forsterite, fayalite, tephroite, monticellite ( $\text{CaMgSiO}_4$ ), and kirschsteinite ( $\text{CaFeSiO}_4$ ) (Deer, Howie, and Zussman, 1962) were

used to calculate  $d_{130}$  spacings as follows: Fo 2.7661, Fa 2.8293, Te 2.8697, Mo 2.9306, Ki 2.9494 Å. Sahama and Hytönen (1958) deduced from data for natural samples the following values for  $d_{130}$ : Fo 2.7659, Fa 2.8328, Mo 2.934, Ki 2.956 Å. Substitution of Ca has the major effect per atom substituted as might be expected from the ionic radii. To bring the observed  $d_{130}$  values for the natural specimens to the equivalent Fo–Fa binary compositions, it may be shown from the calculated  $d_{130}$  spacings that the correction (0.0004Te+0.0022La) in Å should be subtracted from the observed value. This assumes a linear relation between the end members, and that the data for Mo and Ki are averaged to simplify the calculations. Te and La are the mole per cents. of tephroite and larnite. This correction makes a significant change in the appearance of the data (fig. 5) especially for the Fe-rich specimens which contain more Mn and Ca than the Mg-rich ones. The data for the natural specimens fit quite well with the straight line drawn between the values for the synthetic end members. There is a tendency for the corrected values to fall below the straight line (21 are below and 4 are above), suggesting that the true relation between  $d_{130}$  and composition may be slightly non-linear. Two of the specimens which lie above the straight line, R2203 and 39126, are strongly zoned. The probe analyses tend to be made on the centres of the grains where the Mg-content should be greater, thus giving a possible explanation of the upward deviation. However, other specimens such as 60464, 76503, and 76505, are also zoned but do fall in line with the more homogeneous olivines. Specimen YS2 which contains no Mg according to the probe analysis gives a corrected  $d_{130}$  considerably below the value for synthetic fayalite, while specimen YS3 gives a value above the proposed curve for the synthetic specimens. It seems unlikely that the deviation for YS2 can be explained by error in the probe analysis. Perhaps a coupled substitution involving ferric iron modifies the cell dimensions for this specimen. Because the deviations are the result of four factors—error in  $d_{130}$ , error in the probe value for Fo, a difference between the compositions of the five spots used in the probe analyses and the bulk composition estimated by  $d_{130}$ , and deviation from the ideal olivine formula—it is not really possible to do more than set an upper limit to the error in the probe value of Fo. The maximum deviation from a linear relation between the synthetic end members is 4 % in the probe value for Fo. However, in view of the very good internal consistency of the data for the Mg-rich specimens it seems reasonable to suggest that the microprobe estimates of Fo for the natural specimens are accurate to about the 1 % level.

Yoder and Sahama had found that the best straight line for those natural specimens containing little Mn and Ca did not pass within the limits of error through the point for synthetic fayalite. They stated that 'one possible, but improbable, explanation is that two forms of fayalite having slightly different properties exist (see Chudoba and Frechen, 1943). The most likely explanation is that the cell dimensions are a function of the temperature of formation.' The new analyses have permitted a reduction in the scatter of points: in addition, it has been possible to estimate accurately the effect of Ca and Mn. From fig. 5

TABLE IV. Wet chemical analyses

	R1839	R2202	R2203	R2287	39126
SiO <sub>2</sub> ... ..	41.07	30.45	34.42	38.81	34.04
TiO <sub>2</sub> ... ..	0.00	0.19	0.11	0.04	0.43
Al <sub>2</sub> O <sub>3</sub> ... ..	0.09	0.11	0.21	0.38	0.91
Fe <sub>2</sub> O <sub>3</sub> ... ..	0.47	1.15	1.61	1.21	1.46
FeO ... ..	7.42	62.62	41.96	20.18	40.37
MnO ... ..	0.11	1.14	0.63	0.26	0.68
MgO ... ..	50.35	4.14	21.17	39.06	20.32
CaO ... ..	0.00	0.38	0.30	0.09	0.81
H <sub>2</sub> O <sup>+</sup> ... ..	0.12	0.04	0.02	0.16	0.09
H <sub>2</sub> O <sup>-</sup> ... ..	0.00	0.04	0.00	0.04	—
Na <sub>2</sub> O ... ..	n.d.	0.00	0.00	0.00	—
K <sub>2</sub> O ... ..	n.d.	0.00	0.00	0.00	—
NiO ... ..	0.37	n.d.	n.d.	n.d.	—
CoO ... ..	0.01	n.d.	n.d.	n.d.	—
P <sub>2</sub> O <sub>5</sub> ... ..	0.03	n.d.	n.d.	n.d.	—
Total	100.04	100.26	100.43	100.23	99.11

R1839 analysed by J. A. Maxwell and S. S. Goldich, Minn. Rock Analysis Lab., for G. W. DeVore.

R2202, R2203 analysed by E. H. Oslund, Minn. Rock Analysis Lab., for H. M. Gehman, Jr.

R2287 analysed by C. O. Ingamells and D. Thaeplitz, Minn. Rock Analysis Lab., for H. M. Gehman, Jr.

32196 analysed by J. H. Scoon for C. E. Tilley (1952).

it can be seen that there is no longer any need to suppose that there is a systematic difference between natural and synthetic olivines (except for the substitution of Ca and Mn). Nevertheless, the deviation for YS2 suggests that an occasional specimen may have unusual cell dimensions. Possibly the presence of ferric iron may be the cause of such a deviation. Such a suggestion could be tested by synthesizing fayalite over a range of oxidizing conditions.

It seems likely that the relation between  $d_{130}$  and mole per cent. Fo is slightly non-linear with the curve passing near the point  $d_{130}$  2.7965 and

50 % Fo. Such a curved relation is consistent with the conclusion of an extensive discussion by Yoder and Sahama on the applicability of Vegard's 'Law'. To check this suggested curvature it would be of interest to determine  $d_{130}$  for synthetic olivines.

The third test of the microprobe analyses is comparison with the wet chemical analyses. This comparison is uncertain because the wet analyses are for the bulk sample including impurities, whereas the microprobe results refer only to small selected spots on a few grains. Clearly, it is not legitimate to compare the analyses unless a very careful check of impurities has been made. Unfortunately, this is not possible with most of the samples. However, the four samples from the Minnesota Rock Analysis Laboratory occur in large quantities and appear to be effectively pure. For these four specimens there is moderate to good agreement between the wet chemical and the probe results (the wet analyses are reproduced in table IV). Fig. 3 shows the excellent agreement between the two sets of values for Ca and Mn. Table III shows the good agreement between the values for mole per cent. Fo. Ni was determined by wet methods only for specimen 1839; here there is good agreement between the two values. For convenience a summary is given below (the metal values from the wet analyses have been calculated from the reported oxides):

Specimen	Mg <sub>ch</sub>	Mg <sub>pr</sub>	Fe <sub>ch</sub>	Fe <sub>pr</sub>	Ca <sub>ch</sub>	Ca <sub>pr</sub>	Mn <sub>ch</sub>	Mn <sub>pr</sub>	Ni <sub>ch</sub>	Ni <sub>pr</sub>
1839	30.37	30.4	5.77	6.1	0.00	0.00	0.09	0.09	0.29	0.27
2202	2.50	2.2	48.67	49.7	0.27	0.27	0.88	0.91	—	0.02
2203	12.77	12.5	32.62	33.5	0.21	0.20	0.49	0.48	—	0.05
2287	23.56	22.9	15.69	17.0	0.07	0.05	0.20	0.22	—	0.07

Note that Fe<sub>ch</sub> is obtained from both FeO and Fe<sub>2</sub>O<sub>3</sub>.  
ch = chemical; pr = probe.

In the suite of samples collected by Yoder and Sahama some specimens agree very well with the probe results and others disagree seriously.<sup>1</sup> Two specimens, YS25 and YS29, are worthy of special attention because they were hand-picked and because the minor elements were determined

<sup>1</sup> Professor E. A. Vincent of the Dept. of Geology, University of Manchester, has kindly informed us that a forthcoming note in the *American Mineralogist* will record new semi-micro analyses by Dr. J. A. V. Douglas and him on specimens EG5181 and EG5112 which are similar to but not identical with specimens EG1907 and EG4077 listed in table III. The values of  $d_{130}$  for the new specimens are 2.8128 and 2.7944 in close agreement with the values of 2.8126 and 2.7951 found by Yoder and Sahama for the original specimens. The molecular per cents. of Fo derived from the new analyses are 30 and 56 % in moderate agreement with the microprobe values of 26.6 and 52.8 % for the related specimens. It seems reasonable to conclude that the earlier analyses for EG1907 and EG4077 were in error.

by the wet chemical and by optical spectrographic methods. These two are part of the suite of olivines from dunites and inclusions in basaltic rocks carefully described by Ross, Foster, and Myers (1954). The following comparison shows good agreement between the chemical (ch), optical spectrographic (os) and microprobe (pr) analyses:

	Fe <sub>ch</sub>	Fe <sub>pr</sub>	Mg <sub>ch</sub>	Mg <sub>pr</sub>	Mn <sub>ch</sub>	Mn <sub>pr</sub>	Mn <sub>os</sub>	Ca <sub>ch</sub>	Ca <sub>pr</sub>	Ca <sub>os</sub>	Ni <sub>ch</sub>	Ni <sub>pr</sub>	Ni <sub>os</sub>	Co <sub>pr</sub>	Co <sub>os</sub>
YS25	7.98	8.2	29.32	28.9	0.07	0.12	0.12	0.05	0.07	0.0*	0.30	0.28	0.35	0.01	0.016
YS29	6.78	6.7	30.03	29.6	0.12	0.10	0.11	0.05	0.03	0.05	0.31	0.33	0.35	0.01	0.016

\* = not determined.

For the minor constituents Ca and Mn it is possible that the serious discrepancies arise from the presence of impurities in the bulk sample, but it hardly seems likely that impurities cause the large discrepancies for the major components Mg and Fe found for some specimens. The smaller scatter about the curve relating  $d_{130}$  to probe Fo, than that between  $d_{130}$  and chemical Fo, suggests that when there are serious discrepancies between the chemical and probe values for Mg and Fe, these are more likely to result from errors in the wet chemical analyses than from the probe analyses.

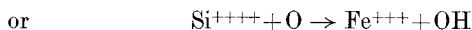
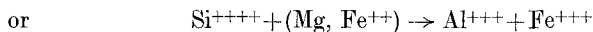
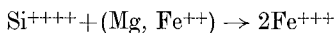
To conclude this portion of the interpretation, evaluation of the error in these microprobe analyses cannot be done with precision; one can only make informed guesses. We suggest that the present data have an error of 1–2 % of the amount present of the Mg and Fe components (except for small values when the error tends towards an absolute value), an error of 2–4 % of the Ca and Mn components (with a minimum value of about 0.01 % of the whole sample), and an error of 0.01 % of the whole sample for Ni and Co. Further refinement of technique should lead to better accuracy for the major components, especially for Mg. The likely sources of error for Mg at the moment are the calibration curve, variable absorption, and correction for drift. Use of scalers instead of a potentiometric recorder will reduce the drift in the recording system. Perhaps it will be possible either to measure or accurately control the beam current, or control the ratio between the beam current and the specimen current (a metal coating may be preferable to carbon, though it may lead to a greater absorption error) thus permitting a smaller effect from beam current variations. Polishing with a finer abrasive such as 0.1 micron alumina or magnesia should lower the absorption error for magnesium, but might produce contamination which would affect the analysis of Mg. Scanning the specimen during analysis should give a better approximation to the bulk composition

than the present procedure of analysing several isolated spots, though there is an increased chance of not recognizing that an impurity has contributed to the analysis. Further homogenization of the reference standards would permit a more accurate determination of the curvature of the calibration. In spite of the deficiencies in the present technique, there is no doubt that it is satisfactory for routine petrographic work, because a 2% error in the major components is often smaller than chemical variations across the mineral grains. Similar accuracies to the ones quoted here are being obtained by us for other silicate groups such as feldspars and pyroxenes. After suitable standards have been prepared there appears to be no reason why all the minerals in a typical rock cannot be analysed for all the major constituents between Na and U in a few hours or, at the most, a few days. If batches of samples are run together there is no reason why analyses of olivines cannot be carried out at the rate of 50 to 100 per hour for each group of three elements. Of course, this assumes that there is no breakdown in the vacuum or electronic equipment of the probe. Unfortunately, it is not possible to determine the valence state of the ions, which is an especial drawback for Fe.

Returning to the specific mineral olivine, two points are of particular interest. First, Ni is often not analysed though the present microprobe results show significant amounts in many specimens, especially the Mg-rich ones. The present analyses show a general increase of Ni with Mg content, as may be expected from theoretical considerations. However, there are exceptions: YS21 and YS24 give low values but both are from meteorites for which low Ni contents in the silicates may be expected. The good agreement between the present data for YS25 and YS29 and the previous wet chemical and optical spectrographic analyses by Ross, Foster, and Myers (1954) shows that the microprobe results for Ni are reliable. Consequently, it is suggested that electron-microprobe techniques will permit rapid determinations of the fractionation of Ni between silicates and sulphides without the need for tedious separation. Häkli (1963), using X-ray spectrographic methods on separated minerals from Finnish peridotites, has shown the value of Ni and other metal determinations in assessing the approach to equilibrium of the mineral assemblages.

Secondly, an important question arises concerning the state of oxidation of iron in olivine. Most olivine analyses carried out by conventional methods show a small part of the Fe in the trivalent form (Deer, Howie, and Zussman, 1962). If olivines are stoichiometric (a reasonable

assumption for a close-packed, tightly-bonded structure)  $\text{Fe}^{+++}$  can enter olivine only as the result of a coupled substitution such as



The amount of  $\text{Al}^{+++}$  listed in chemical analyses is usually small and probably some of it arises from plagioclase or pyroxene impurity. Consequently, the first substitution is the most likely. If this occurs, calculation of the Fa end member from Fe determined by the probe will give too large a value. There is no evidence for such an effect with the present microprobe results; indeed, the totals of the end members are slightly low (99.6 %). It is suggested that some, and perhaps nearly all, of the  $\text{Fe}^{+++}$  reported in olivine analyses is the result of impurities rich in ferric iron, probably the result of oxidation during alteration reactions (see Deer, Howie, and Zussman, 1962, for a summary) or of conversion of ferrous iron to ferric iron during the analytical procedure. Careful measurements should be made to determine the source of the ferric iron in order that its significance in the olivine structure can be determined.

For routine petrographic analysis of olivines, three rapid methods are available which do not involve tedious separation of the minerals. The reflection  $d_{130}$ <sup>1</sup> can usually be recognized in X-ray diffraction patterns even when other minerals are present (Yoder and Sahama, 1957), thus permitting a rapid estimate of the average value of mole per cent. Fo. However, presence of Ca and Mn at the 0.5 to 5 % level leads to serious errors in the estimate. The optic axial angle and refractive indices also permit a rapid estimate of the Mg/Fe ratio: in particular, variation in extinction angle for suitable oriented sections permits a rapid visual study of chemical zoning. Sahama and Hytönen (1958) have shown that a combination of X-ray and optical measurements permits a distinction between specimens in the forsterite-fayalite and monticellite-kirschsteinite series, and also permits estimates of composition. The electron microprobe permits a rapid and accurate estimate of all the major and minor elements in olivine as a function of position in the olivine grain. If transmitted polarized light studies can be made while the specimen is in the electron microprobe (as is possible with the probe

<sup>1</sup> Dr. C. H. Smith has kindly sent us a copy of a paper submitted by Dr. J. L. Jambor and him to the Mineralogical Magazine in which it is shown that the reflection (174) is very suitable for estimation of olivines from small-diameter powder cameras.

built by Dr. J. V. P. Long at Cambridge, and in the A.R.L. and Cambridge Instruments Geoscan commercial microprobes), a rapid correlation between composition and position in the grain can be made. It seems likely that all techniques will find application: for rapid analysis of Mg-rich olivines, for which Ca and Mn are very minor constituents, use of the determinative methods based on  $d_{130}$  or other spacings seems to be quite satisfactory; for routine preliminary surveys, optical studies of olivines in thin sections will continue to have great value, especially as the textural relations can be readily determined at the same time: however, in laboratories with access to the electron microprobe, it seems that a large percentage of the routine analyses will be made by this instrument; furthermore, it can be used for fundamental investigations concerning the composition of minerals and the distribution coefficients of elements between minerals.

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