OLIVINE X-RAY DETERMINATIVE CURVE

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Abstract

The (130) spacing of 31 chemically analyzed natural olivines and seven synthetic olivines has been measured. A determinative curve has been calculated from 26 of the chemically analyzed natural olivines:

$$Fo \ (mol \ \%) = 4233.91 - 1494.59 \ d_{130}.$$

The fictive end points are d_{130} (Fo=100) = 2.7659 and d_{130} (Fo=0) = 2.8328. The error attached to an individual measurement ranges from 3 to 4 mol per cent, depending on the composition.

Portions of the powder x-ray diffraction patterns for synthetic forsterite and synthetic fayalite have been indexed. The cell constants, density, and molar volumes are given.

Introduction

The composition of members of the forsterite-fayalite series may be estimated by measuring the indices of refraction, 2V, or density in lieu of a chemical analysis. The index of refraction and 2V determinative curves of Poldervaart (1950, p. 1073) or Winchell and Winchell (1951, p. 500) are usually used for this purpose. Some prefer to use the index of refraction determinative curve of Bowen and Schairer (1935, p. 197) based on six synthetic olivines, and still others use the 2V tables of Tomkeieff (1939, p. 235), based on Winchell's (1933, p. 191) earlier compilation. Bloss (1952, p. 974–975) gives a determinative curve based on density, using 30 measurements from the literature. It is the purpose of this paper to present a curve for estimating the composition of members of the forsterite-fayalite series using powder x-ray diffraction data.

Method of Investigation

Certain parameters in the structure of olivine vary with composition. These variations may be studied by measuring in a powder x-ray diffraction pattern either the absolute position of reflections or the separation of two reflections from olivines of known composition. The absolute position of a reflection may be determined by measuring the angular separation between the reflection of the olivine and the reflection of an admixed substance whose parameters are known. A plot of either of these data against composition provides a possible means of estimating the composition of unknown olivines.

The measurement of the absolute position of a single reflection was chosen on the basis of the following requirements. (1) A reflection of

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TABLE 1. POWDER X-RAY DIFFRACTION DATA FOR SYNTHETIC FORSTERITE (P-2)

$2\theta_{obs}$	$Q_{obs}\times10^5$	$\Delta Q\times10^5$	hkl	I	d
17.410	3,854	−6	020	26	5.094
20.605	5,382	1	110	3	4.310
22.915	6,640	6	021	95	3.881
23.900	7,214	5	101	39	3.723
25.475	8,180	1	111	13	3.496
25.620	8,272	−3	120	12	3.477
29.865 (α_1)	11,191	−3	002	41	2.989
32.365	13,070	9	130	51	2.766
35.775	15,875	2	131	>100	2.510
36.560 (α_1)	16,583	−8	112	>100	2.456
38.345 (α_1)	18,180	10	041	18	2.345
38.870 (α_1)	18,661	−15	210	8	2.315
39.755	19,453	8	122	50	2.267
40.095 (α_1)	19,808	5	140	48	2.247
41.825 (α_1)	21,475	−31	211	33	2.158
44.560 (α_1)	24,232	39	132	20	2.032
46.800 (α_1)	26,585	−1	042	8	1.940
48.535 (α_1)	28,471	0	150	10	1.874

$2\theta_{obs}$ in degrees: CuKα $\lambda=1.5418$ $Q=1/d^2$

CuKα_1 $\lambda=1.54050$ $\Delta Q=Q_{calc}-Q_{obs}$

d=interplanar spacing in Å I=relative intensity based on arbitrary scale

high intensity throughout the compositional range was sought for two reasons: (a) the intensity diminishes for certain wave lengths of x-radiation (e.g., Cu) with increasing iron content; (b) the amount of olivine in an unknown sample may be small and the intensity will be proportionally reduced. For a high intensity reflection, therefore, olivines need not be carefully separated. In fact it has been found possible to obtain a suitable x-ray pattern from a thin slab or a thin section (with cover glass removed) of some olivine-bearing rocks. (2) The reflection must be resolved clearly from neighboring reflections throughout the range of composition and should be readily distinguishable from those of commonly associated minerals such as plagioclase and pyroxene. (3) The reflection should vary continuously throughout the composition range, preferably uniformly, at a rate suitable for a precise estimate of the composition.

The indices of the observed reflections in the low-angle region for a synthetic forsterite and a synthetic fayalite are given in Tables 1 and 2, respectively. The space group is *Pbnm* (Bragg and Brown, 1926), and the cell dimensions obtained from the powder x-ray diffraction data in Tables 1 and 2 are:

	Synthetic forsterite	Synthetic fayalite
a	4.756±0.005 Å	4.817±0.005 Å
b	10.195±0.005 Å	10.477±0.005 Å
c	5.981±0.010 Å	6.105±0.010 Å

These values are in accord with those published by Rinne (1923, p. 236) and Winchell (1950, p. 14) for samples close to the end members. The density obtained from the cell volumes is 3.222 for forsterite and 4.392 for fayalite. Bloss (1952) gives 3.217 and 4.36 for pure natural forsterite and pure natural fayalite, respectively.

The above requirements appear to be satisfied for the most part by the (130) reflection. It may be noted that none of the adjoining pairs of intense reflections (e.g., 131 and 112) satisfies the conditions desired.

The measurement of the spacing of the (130) reflection was performed in the following way. The sample was ground in an agate mortar under acetone, and about 10 mg. of the olivine powder was mixed with 1–2 mg. of pure silicon powder on a glass slide. A few drops of a very weak solution of lacquer in acetone were added, and then the powder was stirred into a thin film on the slide. The slide was mounted on the Norelco Geiger-counter focusing diffractometer, and records were made on a scale of 1 inch per degree 2θ. The divergent and scatter slits were 1°, receiving slit 0.006 inch, and the scan speed was $\frac{1}{4}$° per minute. The positions of

TABLE 2. POWDER X-RAY DIFFRACTION DATA FOR SYNTHETIC FAYALITE

$2\theta_{obs}$	$Q_{obs}\times10^5$	$\Delta Q\times10^5$	hkl	I	d
16.920	3,642	2	020	16	5.240
20.245	5,197	24	110	8	4.386
22.365	6,328	−1	021	14	3.975
23.515	6,987	6	101	7	3.783
25.050	7,914	−10	111	75	3.555
29.260	10,735	−4	002	11	3.052
31.620	12,491	18	130	100	2.829
34.225	14,568	8	040	22	2.620
34.975	15,195	−3	131	60	2.565
35.915	15,995	−42	112	80	2.500
37.340	17,244	15 / −4	041 / 200	35	2.408
38.300	18,108	43	210	18	2.350
39.080	18,824	62	140	35	2.305
41.205	20,837	−3	211	12	2.191
43.650	23,259	−18	132	6	2.074

$2\theta_{obs}$ in degrees CuKα $\lambda=1.5418$ $Q=1/d^2$
d=interplanar spacing in Å $\Delta Q=Q_{calc}-Q_{obs}$
                          I=relative intensity based on arbitrary scale

the olivine (130) reflection and the silicon (111) reflection were then measured to 0.005° 2θ by a vernier rule. The following standard values of 2θ in degrees for the (111) reflection of silicon were used (Philips Laboratories):

	Kα	Kα_1
Cu	28.465	28.440
Co	33.175	33.150

The position of the olivine reflection was corrected by means of the silicon reflection and the absolute value obtained. The d_{130} values were calculated using 7-place sine tables (Peters, 1918) and the wave lengths for Cu and Co radiation given by Bragg (1947, p. 27).

Four to 12 records of natural and synthetic samples were made by Yoder, using Cu radiation in the region 33–28° 2θ. Five or six records of 17 of the natural samples were made using identical apparatus with Co radiation in the region 38–33° and measured independently by Sahama. These independent data permitted an estimate of operator error since the same sample of silicon powder was used and the same procedures were employed by both authors.

<center>DESCRIPTION OF SAMPLES</center>

Thirty-one analyzed natural and seven synthetic olivines were x-rayed with the Si internal standard. The locality and source of the natural samples are given in Table 3. Chemical analyses of the natural olivines are listed in order of increasing Fo (mol %) content in Table 4. The source and reference to the synthetic samples may be found in Table 5.

The Mg_2SiO_4 content, Fo, of the natural samples was calculated in the following way. The H_2O, F, and alkalies were neglected and the remaining oxides divided by their equivalent weights as given by Stevens (1946, p. 109). These equivalents are adjusted to equal the total of eight anion equivalents of the olivine structure. The resulting numbers are then divided by their respective valence to give the atoms per formula. The Fo content is obtained from the ratio Mg/X of atoms per formula X_2SiO_4. In the past the composition of an olivine has been given on the basis of its iron content, Fa, or if the manganese content, expressed as tephroite, is known and appreciable the composition is recorded as Fo_x-Fa_yTe$_z$. In view of the problems involving the oxidation of iron and manganese, it was considered more appropriate to give the composition in terms of the single-valued component, Fo.

The natural olivines are usually of relatively simple composition (Fo+Fa > 95%) and are, therefore, amenable to the measurement of a single parameter as an estimate of their composition. However, Ca, Al, Fe^{+3}, and Mn may enter the olivines in measurable amounts. Although

TABLE 3. X-Ray Measurements of Natural Olivines

Fo mol %	Original sample No.	Reference No.	Source	Locality	Occurrence	CuKα₁ (Yoder)	CoKα₁ (Sahama)	CoKα₁ (Yoder)	d₁₃₀ Yoder	d₁₃₀ Sahama	av. d₁₃₀
0	USNM90458	18	G. Switzer	Rockport, Mass.	pegmatite in hornblende-biotite granite	31.605 31.595 / 31.610 31.595 / 31.600 31.595	36.830 36.835 / 36.840 36.855 / 36.850 36.830	(36.840)	2.8313	2.8307	2.8310
2.6	EG4139	10,34	I. D. Muir, L. R. Wager	Skaergaard intrusion, Kangerdlugssuak, East Greenland (2600 meters)	olivine-quartz gabbro of layered intrusion	31.615 31.620 / 31.620 31.605 / 31.610 31.630 (31.625)	36.880 36.880 / 36.865 36.870	(36.875)	2.8291	2.8280	2.8286
5.5	F	24	Th. G. Sahama	St. Uttervik Nage, Tunaberg, Södermanland, Sweden	sulpite	31.615 31.610 / 31.625 31.620 / 31.610 31.615 (31.615)	36.840 36.840 / 36.865 36.860	(36.850)	2.8300	2.8320	2.8310
19.2	M3174	17	I. D. Muir	Beaver Bay, Minn.	iron-rich diabase of sill-like intrusion	31.740 31.745 / 31.740 31.745 / 31.760 31.750 (31.745)	—	—	2.8187	—	2.8187
20.2	EG4116	10,34	I. D. Muir, L. R. Wager	Skaergaard intrusion, Kangerdlugssuak, East Greenland (2100 meters)	olivine-quartz gabbro of layered intrusion	31.730 31.720 / 31.720 31.715 / 31.705 31.715 (31.725)(31.715)	—	—	2.8213	—	2.8213
26.3	—	N.P.*	I. D. Muir	Garbh Eilean, Shiant Islands (320 feet above sea level)	olivine-rich dolerite, part of sill	31.765 31.755 / 31.765 31.770 / 31.750 31.760 (31.760)	—	—	2.8174	—	2.8174
32.3	USNM1913	18	G. Switzer	Monroe, Orange Co., N.Y.	with magnetite and calcite	31.935 31.990 / 31.955 31.920 / 31.915 31.920 / 31.930 31.930 (31.930)	37.205 37.205 / 37.220 37.205	(37.210)	2.8028	2.8035	2.8032
39.7	FEAE121	N.P.	K. Hytönen	Noredo, Uganda	olivine diabase	31.890 31.870 / 31.870 31.885 (31.875)	37.160 37.150	(37.150)	2.8075	2.8079	2.8077
40.0	EG1907	10,34	I. D. Muir, L. R. Wager	Skaergaard Intrusion, Kangerdlugssuak, East Greenland (1800 meters)	olivine-quartz gabbro in layered intrusion	31.815 31.815 / 31.815 31.815 / 31.815 31.815 (31.615)	37.135 37.150	—	2.8126	—	2.8126
44.6	—	30	I. D. Muir	Camas Mòr, Muck	olivine gabbro	31.920 31.930 / 31.915 31.915 / 31.905 31.910 31.915 (31.920)	37.310 37.315	—	2.8036	—	2.8036
53.9	E	24	Th. G. Sahama	Susimäki, Vampula, Finland	magnetite-ilmenite olivinite	32.010 32.010 / 32.015 32.005 / 32.005 32.005 (32.010)	37.310 37.335 / 37.315 37.315	(37.315)	2.7959	2.7959	2.7959
55.6	D	24	Th. G. Sahama	drainage channel of Lake Lästilä, Kauklia, Finland	diabase	32.005 32.000 / 32.015 32.025 / 31.990 32.025 (32.005)(32.025)(32.005)	37.305 37.310 / 37.310 37.325	(37.310)	2.7964	2.7963	2.7964
61.3	FEAE62	N.P.	Th. G. Sahama	between Mt. Mbawuru and Mt. Mgahinga, el. 9000 ft., Butumbira, Uganda	phenocrysts in kivite	32.070 32.070 / 32.070 32.060 (32.065)	37.345 37.360 / 37.375 37.355	(37.360)	2.7913	2.7927	2.7920
62.2	FEAE66	N.P.	Th. G. Sahama	Nyarusisa, Bufumbira, Uganda	phenocrysts in diabase	32.060 32.015 / 32.040 32.045 / 32.090 32.045 (32.040)	37.385 37.385 / 37.400 37.370	(37.385)	2.7934	2.7908	2.7921
63.1	EG4077	10,34	I. D. Muir, L. R. Wager	Skaergaard Intrusion, Kangerdlugssuak, East Greenland (500 meters)	olivine-hypersthene gabbro of layered intrusion	32.025 32.090 / 32.000 32.015 / 32.025 32.025 (32.020)	—	—	2.7951	—	2.7951

TABLE 3. X-RAY MEASUREMENTS OF NATURAL OLIVINES—(Continued)

io mol %	Original sample No.	Reference No.	Source	Locality	Occurrence	Measurements of 2θ(130) CuKα (Yoder) (Average in parentheses)	CoKα₁ (Sahama)	d₁₃₀ Yoder	d₁₃₀ Sahama	av. d₁₃₀
68.1	FEA574	N.P.	Th. G. Sahama	Congo frontier on the road, Bufumbira, Uganda	phenocrysts in diabase	32.080 / 32.090 / 32.080 / 32.105 / 32.110 / (32.095)	37.415 / 37.440 / 37.420 / 37.435 / 37.445 / 37.430 / (37.430)	2.7887	2.7877	2.7882
73.9	—	15	S. R. Nockolds	Kimanzoogda, Farm Goedemond Annexe, Robertson District, Cape Province, South Africa	phenocrysts in melilite basalt	32.155 / 32.145 / 32.150 / 32.120 / 32.145 / 32.160 / (32.130) / (32.145)	—	2.7845	—	2.7845
76.4	II	N.P. (see 13)	R. Johnston	Garbh Eilean Sill, Shiant Islands (38 ft. above sea level)	picrodolerite part of sill	32.170 / 32.185 / 32.175 / 32.175 / 32.180 / 32.180 / 32.195 / 32.180 / (32.180)	—	2.7816	—	2.7816
78.0	I	N.P. (see 13)	R. Johnston	Garbh Eilean Sill, Shiant Islands (sea level)	picrite, base of sill	32.195 / 32.205 / 32.190 / 32.210 / 32.190 / 32.210 / 32.205 / (32.200)	—	2.7799	—	2.7799
80.6	FEA6139	N.P.	K. Hytönen	Merollinga, Karamoja, Uganda	phenocrysts in volcanic limburgite neck	32.220 / 32.210 / 32.215 / 32.230 / (32.220)	37.555 / 37.545 / 37.555 / 37.540 / 37.555 / 37.545 / (37.550)	2.7782	2.7791	2.7786
80.8	BM1932.9	28	M. H. Hey	Allen Springs, Australia	meteorite	32.270 / 32.260 / 32.285 / 32.290 / 32.270 / 32.285 / (32.275)	37.630 / 37.615 / 37.625 / 37.615 / 37.630 / 37.620 / (37.620)	2.7736	2.7741	2.7738
85.6	—	15	S. R. Nockolds	Spiegel River, Riversdale District, Cape Province, South Africa	phenocrysts in melilite basalt	32.240 / 32.265 / 32.275 / 32.235 / 32.235 / 32.265 / (32.250)	—	2.7757	—	2.7757
87.4	FEA356	N.P.	Th. G. Sahama	Muko Flow, Rubanda Area, Uganda	phenocrysts in ugandite	32.280 / 32.275 / 32.260 / 32.255 / 32.270 / (32.270)	37.615 / 37.600 / 37.610 / 37.605 / 37.605 / 37.600 / (37.605)	2.7740	2.7751	2.7746
87.8	C	24	Th. G. Sahama	Marjalahti, Finland	meteorite	32.270 / 32.285 / 32.270 / 32.270 / 32.290 / 32.280 / 32.260 / 32.285 / (32.275)	37.630 / 37.630 / 37.625 / 37.620 / 37.625 / 37.635 / (37.625)	2.7736	2.7737	2.7736
88.4	7	22	C. S. Ross	Ichinomegata, Akita Prefecture, Japan	nodule in basalt	32.290 / 32.275 / 32.275 / 32.270 / 32.280 / 32.280 / 32.265 / (32.275)	37.645 / 37.640 / 37.650 / 37.650 / 37.640 / 37.655 / (37.650)	2.7736	2.7720	2.7728
88.6	III	11	R. Johnston	Ubekendt Island, West Greenland	intrusive picrite sheet	32.300 / 32.270 / 32.280 / 32.305 / 32.275 / 32.305 / 32.290 / (32.290)	—	2.7723	—	2.7723
89.9	B	24	Th. G. Sahama	Ultenthal, Tyrol, Austria	dunite	32.275 / 32.285 / 32.285 / 32.280 / 32.285 / 32.310 / (32.285)	37.635 / 37.620 / 37.625 / 37.610 / 37.635 / 37.615 / (37.625)	2.7727	2.7732	2.7730
90.1	A	24	Th. G. Sahama	Dreis, Eifel, Germany	volcanic bomb	32.295 / 32.300 / 32.280 / 32.295 / 32.300 / 32.295 / 32.295 / 32.290 / 32.315 / (32.295)	37.645 / 37.650 / 37.660 / 37.645 / 37.655 / 37.640 / (37.650)	2.7719	2.7720	2.7720
90.4	8,USNM53948	22	C. S. Ross	Salt Lake Crater, Oahu, Hawaii	nodule in basalt	32.295 / 32.295 / 32.300 / 32.290 / 32.280 / 32.285 / 32.280 / 32.295 / (32.290)	37.660 / 37.655 / 37.675 / 37.660 / 37.655 / (37.660)	2.7723	2.7712	2.7718
91.1	14	22	C. S. Ross	Noumea, New Caledonia	serpentinized peridotite	32.310 / 32.280 / 32.290 / 32.295 / 32.310 / (32.295)	37.645 / 37.650 / 37.630 / 37.655 / 37.655	2.7719	2.7718	2.7718
94.7	150	23	Th. G. Sahama	Ojamo, Lohja, Finland	limestone, with clinohumite	32.330 / 32.325 / 32.320 / 32.325 / 32.325 / 32.325 / 32.320 / 32.315 / (32.320)	37.710 / 37.690 / 37.710 / 37.720 / 37.700 / 37.700 / (37.705)	2.7698	2.7680	2.7689

ᵃN.P. = chemical analysis not published.

there appear to be narrow limits within which the first three atoms may substitute, Mn is known to form a complete series of solutions, fayalite-tephroite. For these reasons certain restrictions had to be placed on the composition of olivines used to construct the determinative curve. Only specimens whose analyses satisfied the following specifications of atoms per formula were considered suitable for a determinative curve:

Si: 0.97–1.03
X: 1.93–2.04
Mn: 0–0.03

TABLE 4. CHEMICAL ANALYSES OF NATURAL OLIVINES

Fo mol %	Theoretical 0.0	0.0	2.6	5.5[a]	19.2	20.2[b]	26.3[c]	32.3	39.7	40.0	44.6
SiO_2	29.48	30.08	30.15	29.96	30.42	31.85	31.56	33.77	34.08	33.72	34.04
TiO_2		n.d.	0.20	0.00	1.20	0.01	0.41	n.d.	0.04	tr.	0.43
Al_2O_3		n.d.	0.07	0.00	0.50	tr.	0.79	n.d.	0.00	nil	0.91
Fe_2O_3		n.d.	0.43	0.00	nil	0.11	n.d.	n.d.	0.27	0.05	1.46
FeO	70.52	68.12	65.02	63.31	57.62	58.64	53.64	47.26	47.30	47.91	40.37
MnO		0.72	1.01	4.40	n.d.	0.85	0.56	4.54	0.65	0.41	0.68
MgO		n.d.	1.05	2.23	8.17	8.49	11.39	13.88	17.83	18.07	20.32
CaO		n.d.	2.18	0.10	1.32	0.18	0.85	n.d.	0.00	nil	0.81
H_2O^+	} 0.88		n.d.	0.00	0.18	n.d.	0.16	} 0.48	0.05	n.d.	} 0.09
H_2O^-			n.d.	0.00	0.21	n.d.	0.06		0.00	n.d.	
Total	100.00	99.80	100.11	100.00	99.62	100.13	99.42	99.93	100.22	100.16	99.11

Fo mol %	53.9[d]	55.6[e]	61.3	62.2	63.1	68.1	73.9	76.4	78.0	80.6[f]	80.8
SiO_2	35.31	35.84	36.25	36.28	38.11	37.76	37.33	37.93	38.07	38.53	37.24
TiO_2	0.00	0.00	0.00	0.00	tr.	0.00	0.09	tr.	0.07	0.04	nil
Al_2O_3	0.00	0.00	0.14	0.10	nil	0.04	0.18	0.11	0.03	0.74	n.d.
Fe_2O_3	1.70	1.99	0.64	0.00	0.15	0.40	1.60	0.02	0.01	0.67	n.d.
FeO	36.91	35.18	32.60	32.90	31.48	27.66	21.58	21.70	19.95	16.60	16.92
MnO	0.53	0.60	0.26	0.22	0.22	0.11	0.27	0.16	0.25	0.27	n.d.
MgO	25.55	26.39	30.04	30.75	30.50	34.05	38.13	40.40	41.20	43.15	43.88
CaO	0.00	0.00	0.12	0.05	0.02	0.16	0.38	0.17	0.27	0.00	1.26
H_2O^+	0.00	0.00	0.00	0.00	n.d.	0.00	0.17	n.d.	} 0.03	0.00	n.d.
H_2O^-	0.00	0.00	0.00	0.00	n.d.	0.00	0.04	n.d.		0.00	n.d.
Cr_2O_3	0.00	0.00	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
P_2O_5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.09	n.d.	n.d.	n.d.	n.d.
Na_2O	} 0.00	} 0.00	n.d.	n.d.	n.d.	n.d.	0.03	n.d.	n.d.	n.d.	n.d.
K_2O			n.d.	n.d.	n.d.	n.d.	0.05	n.d.	n.d.	n.d.	n.d.
Total	100.00	100.00	100.05	100.30	100.48	100.18	99.94	100.49	99.88	100.00	99.30

TABLE 4. CHEMICAL ANALYSES OF NATURAL OLIVINES—(Continued)

Fo mol %	85.6	87.4	87.8	88.4	88.6[g]	89.9[h]	90.1	90.4	91.1	94.7	Theoretical 100.0
SiO_2	39.12	40.90	40.24	40.30	39.81	40.72	40.60	40.87	41.32	41.07	42.69
TiO_2	0.09	0.00	0.00	0.15	tr.	0.12	0.00	0.02	0.01	0.05	
Al_2O_3	0.58	0.25	0.01	0.25	nil	0.09	0.20	0.07	0.00	0.56	
Fe_2O_3	1.69	0.66	0.68	0.00	nil	0.10	0.96	0.00	0.30	0.65	
FeO	10.76	10.73	10.92	10.26	10.20	9.48	8.35	8.72	7.49	3.78	
MnO	0.16	0.20	0.28	0.09	0.13	0.13	0.16	0.15	0.15	0.23	
MgO	46.51	46.96	48.08	48.60	49.03	49.52	49.60	49.78	49.56	54.06	57.31
CaO	0.48	0.14	0.00	0.07	0.75	0.00	0.00	0.07	0.29	0.00	
H_2O^+	0.21	0.06	0.00	} 0.33	n.d.	0.00	0.00	} 0.05	} 0.60	0.05	
H_2O^-	0.07	0.00	0.04		0.04	0.02	0.04			0.00	
F	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.00	
Cr_2O_3	n.d.	n.d.	0.07	0.03	n.d.	0.03	0.03	0.02	0.04	n.d.	
P_2O_5	0.07	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Na_2O	0.15	n.d.	} 0.00	0.04	n.d.	} 0.00	} 0.00	0.01	0.01	n.d.	
K_2O	0.06	n.d.		0.03	n.d.			0.00	0.00	n.d.	
NiO	n.d.	n.d.	n.d.	0.41	n.d.	n.d.	n.d.	0.34	0.31	n.d.	
CoO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.013	0.011	n.d.	
Total	99.95	99.90	100.32	100.56	99.96	100.21	99.94	100.11	100.09	100.45	100.0

a. Corrected for an estimated 1% magnetite.

b. Analyzed specimen was incorrectly referred to as EG4145 (Wager and Deer, 1939, p. 73). See Wager and Deer (1939, p. 71) and Deer and Wager (1939, p. 23).

c. Partial analysis.

d. Corrected for estimated 0.75% ilmenite and magnetite.

e. Corrected for estimated 2% analyzed titanomagnetite.

f. Corrected for 1.6% analyzed clinopyroxene.

g. Spectrographic determinations in p.p.m. given by S. R. Nockolds: Cr, 1000; V, 5; Ni, 1750; Co, 120.

h. Value for Al_2O_3 misprinted as 0.90.

The following specimens were rejected on the basis of their chemical analyses:

Mol % Fo	Locality	Basis for rejection
80.8	Alice Springs, Australia	low Si, high X
32.3	Monroe, Orange County, N. Y.	high Mn
5.5	St. Utterviks Hage, Tunaberg, Sweden	high Mn

The rejected specimens will be reconsidered in the light of their (130) spacing below.[1]

[1] It would be desirable to construct a determinative grid for the series forsterite-fayalite-tephroite based on d_{130} and some other parameter (e.g., index of refraction, $2V_\alpha$, density); however, a sufficient number of suitable analyzed specimens were not available. It is noteworthy that the variation of d_{130} is unique relative to the nearly parallel variations of indices of refraction, $2V_\alpha$, and density.

TABLE 5. X-RAY MEASUREMENTS FOR SYNTHETIC OLIVINES

Name	No.	Reference	Source	Preparation	Measurements of 2θ(130)					d
							CuKα			
Forsterite	T2-36C	5	O. F. Tuttle	hydrothermal	32.375	32.380	32.360	32.380	32.355	2.7657
					32.345	32.370	32.370	32.380	(32.370)	
Forsterite	P-2	38	H. S. Yoder	hydrothermal	32.365	32.350	32.350	32.360	(32.355)	2.7669
					32.355	32.360	32.370			
Forsterite	—	—	J. F. Schairer	dry fusion	32.370	32.375	32.375	32.355	(32.370)	2.7657
					32.375	32.365	32.375	32.370		
Fayalite	—	2	L. H. Adams	blast furnace	31.620	31.630	31.610	31.615	(31.620)	2.8295
					31.625	31.625	31.610	31.635		
Fayalite	—	14	Th. G. Sahama	dry fusion	31.630	31.630	31.625	31.610	(31.625)	2.8291
					31.635	31.620	31.630	31.630		
Fayalite	FAS112-2	26	K. Yagi	dry fusion	31.625	31.610	31.635	31.630	(31.620)	2.8295
					31.635	31.620	31.615	31.610		
Tephroite	—	27	R. B. Snow	dry fusion	31.165	31.170	31.150	31.160	(31.165)	2.8698
					31.160	31.180	CoKα₁			
Fayalite	—	14	Th. G. Sahama	dry fusion	36.870	36.875	36.850	36.850	(36.860)	2.8292
					36.860	36.860				

RESULTS FROM NATURAL SPECIMENS

The x-ray data for the natural samples are given in Table 3 and the average values (the mean of the average for those x-rayed by each writer) are plotted in Fig. 1.

Two points in the figure, in addition to two of those rejected on the basis of chemical analysis, are almost certainly subject to large error:

Mol % Fo	*Locality*
40.0	East Greenland 1907 (1800 meters)
63.1	East Greenland 4077 (500 meters)

The first of these has been reexamined optically by Dr. I. Muir and he gives Fo$=25$–27 on the basis of indices of refraction ($\gamma=1.829$) and $2V_\alpha(60°)$. The value obtained from the x-ray measurement is Fo$=30$. Since there appears to be agreement between the new optical and x-ray determinations, the chemical analysis is believed to be in error and is re-
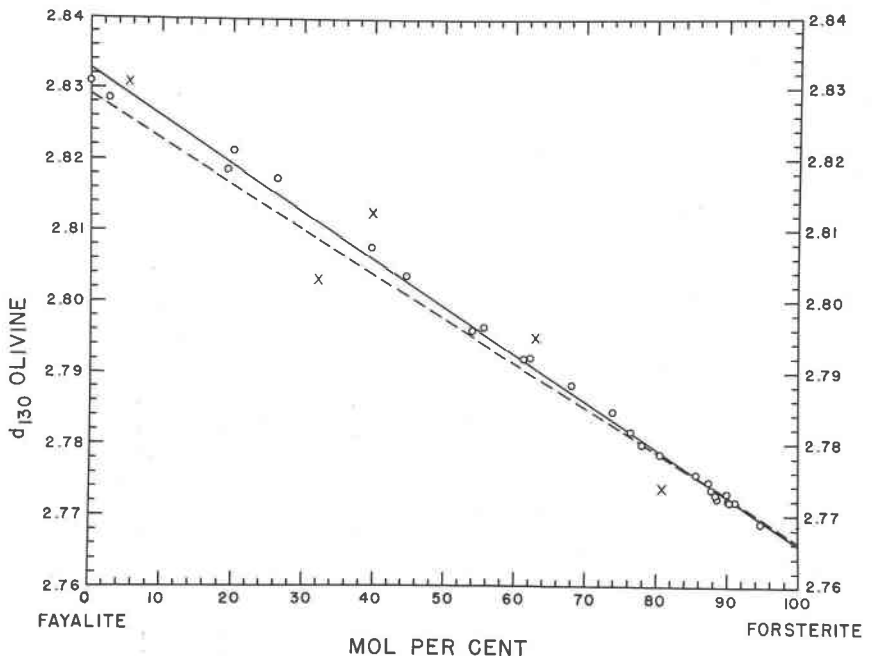
FIG. 1. Olivine x-ray determinative curve (solid line). Circles represent average d_{130} for analyzed specimens used in calculation of determinative curve. Crosses represent those points rejected for reasons given in text. Dashed line is assumed linear variation of d_{130} for synthetic olivines, using experimentally determined end points.

jected. There are no obvious reasons for rejecting the chemical analysis of the second specimen. The writers have taken the liberty of excluding this measurement from the calculation of the determinative curve for the sole reason that it appears to be anomalous.

Other problems arose in fitting a curve to the data on the natural specimens, and the writers are indebted to Dr. Felix Chayes for suggesting the following statistical analysis and making many of the computations.

The first problem to arise involved the use of the data obtained by each writer on the same specimen. It was necessary to learn whether either group of averaged measurements was biased before they could be combined. The spacing data for those compositions x-rayed by both writers were plotted against each other. If there were no bias the best fitting straight line would be characterized by a slope not differing significantly from unity and an intercept not significantly different from zero (see Youden, 1951, p. 40–49). The following equations were obtained using first the spacings of Yoder (d_y) and then those of Sahama (d_s) as the independent variable:

$$d_s = 1.0105 \, d_y - 0.00117$$
$$d_y = 0.9868 \, d_s + 0.00142.$$

For the first equation the error of slope is 0.0140 and that of the intercept 0.00130. The errors for the constants of the second equation are 0.0136 and 0.00127, respectively. Departures of slopes and intercepts from the expected values are thus insignificant in relation to error, and it is permissible to use the mean of the average d value of each writer. In a broader sense, the small differences between the two equations also indicate that analogous measurements by other investigators may be compared with those presented here in estimating the composition of unanalyzed olivines.

Next, it was necessary to choose the independent variable, d_{130} or composition. The spacing was chosen as the independent variable for two reasons: (1) in the opinion of the writers the d_{130} is known better than the chemical composition, which is based on only a single analysis of each specimen, and (2) the spacing is to serve as the estimator of the chemical composition in the application of the determinative curve.

The equation of the determinative curve for the data assembled in the above-mentioned fashion is

$$Fo \ (mol \ \%) = 4233.91 - 1494.59 \, d_{130}.$$

The residual variance amounts to 0.34%, and, as there seems to be no systematic distribution of deviations, higher order terms are not justified.

The fictive end points are d_{130} (Fo $= 100$) $= 2.7659$ and d_{130} (Fo $= 0$) $=$ 2.8328.[1]

The upper and lower 95 per cent confidence limits are as follows:

d	True value, mol % Fo	±95% confidence limits
2.8328	0	1.65
2.8194	20	1.23
2.8061	40	0.88
2.7994	50	0.74
2.7927	60	0.69
2.7793	80	0.76
2.7659	100	1.08

The confidence limits plot as gentle curves, which are closest to the determinative curve at its mean and furthest from it at the limits of the range. The strict interpretation of the confidence limits presupposes that d is subject to negligibly small random errors. As seen in the data tables the estimate of d is subject to measurable error. The standard deviation is 0.00084 Å, and since the total range is only 0.0669 Å this amounts to ± 2.45 mol per cent Fo. If the errors involved in the estimate of d_{130} and the estimate of the true composition are added, the error attached to an individual estimate of composition, using the above determinative curve, is approximately ± 4 mol per cent near pure Fo or Fa and about ± 3 mol per cent in the vicinity of the mean, which lies near 64 mol per cent Fo.

RESULTS FROM SYNTHETIC SPECIMENS

The average d_{130} for the three synthetic forsterite specimens and three synthetic fayalite specimens is 2.7661 and 2.8293, respectively. On the assumption that the variation of d_{130} is linear throughout the composition range, the following determinative curve may be calculated:

$$\text{Fo (mol \%)} = 4476.739 - 1582.278 \, d_{130}.$$

The validity of the assumption will be examined below. The curve is plotted as a dashed line in Fig. 1.[2]

The d_{130} for synthetic tephroite is 2.8697. The value is included for use in determining the correction for olivines high in Mn.

[1] In the Annual Report of the Director of the Geophysical Laboratory (Abelson, 1954, p. 120) the fictive end points of the preliminary curve based on fewer data were given as d_{130} (Fo $=100$) $=2.7660$ and d_{130} (Fo $=0$) $=2.8326$.

[2] The synthetic intermediate olivines prepared by Bowen and Schairer (1935, p. 195–197), on which the optical determinative curves are based, could not be located. Only the unanalyzed, partially oxidized starting materials prepared in the gas furnace were found, and these gave broad multiple reflections.

DISCUSSION OF RESULTS

Those samples rejected on the basis of their chemical analysis may now be reexamined in the light of their (130) spacings. The Alice Springs, Australia, specimen (Fo = 80.8) appears to have too small a spacing. The discrepancy cannot be attributed to the Ca or Mn (not determined) content since the correction would have the wrong sign. The analysis is still regarded as incorrect. The Monroe, Orange County, N. Y., specimen (Fo = 32.3) was considered to have too high an MnO content (4.54%); however, the correction for Mn would be in the wrong direction. The olivine occurs with magnetite, and it is possible that inclusions of that mineral could account for too high an FeO content (Fe_2O_3 was not determined). The St. Utterviks Hage, Tunaberg, Sweden, specimen (Fo = 5.5) was also believed to have too high an MnO content (4.40%) to be suitable for a determinative curve of the forsterite-fayalite series. When corrected for Mn, however, the spacing still gives a reasonable estimate of the Fo content.

The two additional specimens rejected, East Greenland 1907 (Fo = 40.0) and East Greenland 4077 (Fo = 63.1), have (130) spacings which indicate high Mn content. The chemical analyses do not support this suggestion.

The difference (0.0035 Å) between the d_{130} of synthetic fayalite and the fictive d_{130} for pure natural fayalite lies outside the precision of measurement and is of some concern. The fictive point represents a fayalite having 8.7 mol per cent tephroite or 6.0 weight per cent MnO, on the assumption that the (130) spacing of synthetic fayalite is correct. Since the chemical analyses of the natural samples were chosen on the basis of low MnO content, the source of the discrepancy must lie elsewhere. 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 synthetic fayalites were produced at temperatures over 1000° C. Olivines having a high iron content are usually associated with lower temperatures. It is to be noted that there is close agreement between the (130) spacing of synthetic forsterite and the fictive (130) spacing for a pure natural forsterite.

THEORETICAL RELATION OF d_{130} TO COMPOSITION

The practical problem of estimating the composition of most natural olivines by means of d_{130} appears to have been met. It is of interest to examine qualitatively why d_{130} varies linearly, within the limits of error, with composition.

The construction of a compositional determinative curve for solid solution series from powder x-ray diffraction data was suggested and applied to certain cubic systems by Vegard (1921) and further applied by Vegard and Dale (1928). Vegard's "law" stated that the cell dimension, a_0, varied linearly with composition. Deviations from linearity were considered as a measure of the nonideality of the solid solution series. Grimm and Herzfeld (1923, p. 80) as well as Mehl and Mair (1928, footnote p. 65) and Zen (1956) pointed out that it is the atomic volume, a_0,[3] which varies linearly in *ideal* substitutional type solid solutions. Further complications arose when the "law" was applied to systems of lower symmetry since two or more parameters had to be considered. For these reasons Vegard's "law" is now used only in special cases as an approximation.

The forsterite-fayalite series has been shown in part to be thermodynamically ideal within the error of measurement by Sahama and Torgeson (1949) on the basis of heats-of-solution data. In addition, the present writers find that the molar volumes of natural olivines calculated from the density data of Bloss (1952, p. 974–975) are essentially additive. (The molar volumes of synthetic forsterite and synthetic fayalite, 43.7 cc. and 46.4 cc., respectively, calculated from the unit cell data of Tables 1 and 2, differ by only a small amount.) These observations suggest that the variation of cell parameters should not deviate greatly from the ideal values.

There is, unfortunately, no unique way of predicting the changes of a specific cell spacing solely from knowledge of the additivity of molar volume. The cell volume, V, is related to the molar volume V_m by a constant:

$$V = \frac{nM}{N_0 \delta} = kV_m,$$

where n = molecules per unit cell, N_0 = Avogadro's number, δ = density, M = molecular weight; and is related to the three parameters of the orthorhombic cell by

$$V = abc.$$

On the other hand, the spacing of any (hkl) is related to the orthorhombic cell parameters as follows:

$$d_{hkl} = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{-1/2}.$$

The relation of d_{130} to the cell parameters would then be

$$d_{130} = \left(\frac{1}{a^2} + \frac{9}{b^2} \right)^{-1/2}.$$

If one notes that a/b is approximately the same for the olivine end members, then the change of d_{130} with composition is essentially a linear func-

tion of the parameters. It is presumed that the total change of each cell parameter is sufficiently small over the composition range so that their functions are closely approximated by straight lines. An examination of the Bunn chart (Bunn, 1946, p. 133) for indexing tetragonal powder patterns indicates that the variation of d_{hkl} is essentially linear for small changes in the axial ratio. On the basis of these qualitative arguments the linear relation of d_{130} vs. composition appears reasonable.

In conclusion, certain features of the x-ray method should be pointed out. The peak observed on an x-ray chart is a summation of the diffraction of many crystals. If these crystals are variable in composition, as a result of zoning, for example, then a broad peak or even a multiple peak obtains. The x-ray method, therefore, gives an average composition in the same way as a chemical analysis, but in addition indicates in a crude way the range. On the other hand, composition determined by optical methods represents that of a small number of crystals, and some discrepancies between the results of the various methods are to be expected. Although the variations in the three cell parameters of natural olivines may not be sufficiently unique, it should be possible to determine composition of crystals in the three-component system forsterite-fayalite-tephroite by means of powder x-ray diffraction patterns. It is more likely that a combination of methods, optical and x-ray, will provide a more practical estimate of composition of the complex olivines.

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