

Phenocrystic olivines from the eastern Azores

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SUMMARY. Phenocrystic and xenocrystic olivines and one olivine nodule sample, all from volcanics in the eastern Azores, range in composition from Fo₈₇ to Fo₆₉. Most are phenocrysts from the Nordeste alkali basaltic complex, eastern São Miguel Island, in which olivine-bearing rocks range from ankaramite to latite. CaO, MnO, and NiO trends are related to Mg-Fe contents, both for the concentrates as a whole, and also within analysed zoned crystals. It is shown that anomalous plots of $\Delta 2\theta(220_{\text{LIF}} - 062_{\text{olivine}})$ are related to pronounced Mg-Fe zonal gradients and, in samples from some flows, to mixtures of different generations of olivine. Regressions of $\Delta 2\theta$ vs. Fo (mol %) and FeO (wt %) for the least-zoned olivines are in close accord with those for Hawaiian olivines reported by Murata and others (1965).

MnO percentages increase linearly with FeO; this and the Hawaiian trend are indistinguishable. Limited data for the most magnesian olivines indicate that NiO increases with FeO up to ~ 15 wt % of FeO; the trend then decreases with further iron enrichment. This trend is apparent from other olivine data, and its relationship to the onset of pyroxene crystallization is discussed. CaO in olivine phenocrysts is inversely related to normative anorthite percentages in host rocks; the trend appears to be controlled largely by co-precipitation and fractionation of calcic plagioclase.

MINOR-ELEMENT contents in olivines have received increasing attention, not only with regard to correlation with lattice parameters and other physical properties, but also because minor-element trends and their zonal gradients within crystals can potentially contribute much to petrologic interpretation of the early crystallization histories of basaltic liquids. Studies by Jackson (1960), Hotz and Jackson (1963), and Murata, Bastron, and Brannock (1965) were concerned with establishing X-ray working curves for olivines in plutonic and volcanic environments. Their regressions of major end-member compositions against X-ray values differ chiefly because of the greater percentages of Ca and Mn (or larnite and tephroite end-members) in olivines (Fo₈₈₋₇₆) quenched at volcanic solidus temperatures. Murata and others (1965, p. C36) noted, however, that olivines from peridotitic xenoliths in Hawaiian volcanics obeyed the 'volcanic' regression line in accord with phenocrystic olivines from several flows.

During a study of the chemistry and mineralogy of Azores alkali basalts and related differentiates, the opportunity arose to further define the characteristics of olivine phenocrysts under volcanic conditions. Fernandez mapped the Nordeste Basaltic Complex on the east end of São Miguel Island (1969), and we have also visited other localities in the eastern part of the Azores archipelago. Our investigation relates chiefly to the Nordeste volcanics because unaltered phenocrystic olivine occurs widely throughout the eruptive sequence of the shield complex, and because we can relate olivine crystallization behaviour to that of the host-rocks and other coexisting phenocrystic phases. We first set out to learn if the 062-related regression line for

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Hawaiian phenocrysts would apply to those in the Azores rocks we have studied. The unexpected abnormal plots of many of the X-ray values against bulk composition of phenocryst concentrates led us to examine the zoning of the olivines as a principal cause. We discuss this further below.

Louisnathan and Smith (1968) have shown that the unit cell parameters of low-calcium natural olivines can be adjusted to those corresponding to the pure Fo-Fa series by linear equations using appropriate constants for the molar proportions of larnite and tephroite. Their constants, as modified for the 062 lattice spacing, are used with a provisional constant for Ni in five of our most homogeneous, least-zoned concentrates. Using Louisnathan and Smith's assumptions concerning olivine stoichiometry (1968, p. 1125), the equation can be used to deduce the precision of calcium analysis in olivines for which accurate 062 measurements, or unit cell data, have been obtained. Implicit in its use is the further assumption that Ca is randomly distributed in the octahedral sites.

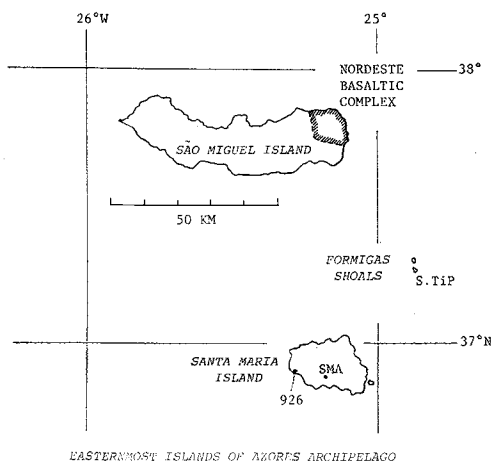


FIG. 1. Locations of analysed olivines. Details of localities in table I.

Wyllie (1960) has pointed out some of the petrologic implications of the effect of Ca in lowering the liquidus and solidus temperatures in the orthosilicate plane of the system CaO-MgO-FeO-SiO_2 . Kushiro and Schairer (1963) have demonstrated concentrations of nearly 3 wt % CaO in olivine in their restudy of the system Fo-Di-SiO_2 . Presnall (1966) reported 1 mol % larnite in olivines under solidus conditions in the system Fo-Di-iron-oxide . If entry of Ca into natural olivines increases with iron enrichment, as one might expect from comparison of ionic radii, then CaO should plot in some continuously positive manner against FeO. Our data, however, show that this is not followed by the Azores olivines. We therefore discuss preliminary olivine-whole-rock relationships that suggest entry of Ca in olivine is affected by cotectic plagioclase crystallization.

Description. The phenocrystic olivines in ankaramites and olivine-rich trachybasalts from the Nordeste complex, eastern São Miguel, are unusually large, up to 24 mm long. Those in other rock types from this complex and from basalts on Santa Maria Island and Formigas Shoals are rarely larger than 3 mm. Most of the olivines are euhedral to subhedral. Olivine in the Nordeste complex is remarkably unaltered and free of inclusions, only a small proportion containing grains of Cr-bearing Fe oxide embedded near the rims. Pronounced zoning in coexisting pyroxene phenocrysts suggested that the olivines should similarly be zoned. On examining several large

olivine phenocrysts in thin-section on the universal stage following Tomkeieff's procedure (Tomkeieff, 1939), we discovered that most were strongly zoned (Esenwein, 1929, also noted zoning in Azores olivines). Zoning is also expressed by variations in 2V and by X-ray diffraction line broadening, and is further confirmed by electron-probe multiple-point analyses. Some of the larger euhedra have rounded cores and may owe their origin to partial resorption of early formed olivine around which a more Fe-rich mantle was precipitated in optical continuity. Other evidence of coexisting multiple generations of olivine are glomerocrystic clusters of olivines associated with clinopyroxenes and iron oxides, in addition to a groundmass olivine phase. We have not analysed the groundmass olivines. Le Maitre (1962) stated that olivine in Gough Island volcanics lacks notable zoning, yet in other aspects of mineralogy and chemistry the Gough Island alkali basalts are similar to those of the eastern Azores (Fernandez, 1969). Forbes and Banno (1966) analysed for Fe and Ni across zoned cognate olivines in alkali basaltic volcanics and demonstrated an inverse relation between Fe and Ni across the gradational trend of normal zoning. Muir and Tilley (1964) noted Fe-rich rims on otherwise unzoned xenocrysts and strongly zoned microphenocrysts in tholeiitic basalts from the Mid-Atlantic Ridge. White (1966) also noted Fe-enrichment at rims of phenocrystic olivines in olivine tholeiites.

Analytical procedures. Hand-separated phenocrysts were first examined for purity and lack of alteration under a binocular microscope. Olivine was easily distinguished from chromediopside and titanite. After grinding the phenocryst concentrates under acetone in a tungsten carbide mortar to < 200 mesh, oxides and oxide-contaminated grains were removed in an isodynamic separator. The resulting 17 purified concentrates were split for chemical and X-ray study. We analysed each concentrate for the common cations in octahedral co-ordination in olivine: Mg, Fe, Ca, Mn, and Ni. We determined concentrations by atomic absorption spectrophotometry immediately after the olivines were put into solution following the LiBO₂ fusion procedure (Suhr and Ingamells, 1966). We also analysed for Mg and Fe by the same spectrophotometric method after dissolving a second split of the olivines in an HF, H₂SO₄, and HNO₃ solution (Shapiro and Brannock, 1962). Results for the two principal elements by both methods were closely comparable. Dilutions for each element were monitored by weight. Standard solutions were interspersed with unknowns during the runs as a check on instrumental drift. Results are listed in table I.

Analyses were checked by using the standard stoichiometric relation to SiO₂ and assuming that all the analysed elements are octahedrally co-ordinated in olivine. Only eight analyses yield totals, by stoichiometric reconstruction, that are between 99.1 and 100.2 wt %; 8 are between 100.5 and 102, and one gives a low total of 98.1. This is noteworthy, as we have found that partial analyses reported on this stoichiometrically simple mineral yield calculated end-member totals that range surprisingly wide of 100 %. Our totals are generally higher for Mg-rich concentrates, implying analytical error the source of which we cannot presently explain. Smith (1966) reported the same effect.

X-ray experimental procedure. Diffractometer settings were equivalent to those used by Jackson (1960) and Murata and others (1965): $\lambda = \text{Cu-K}\alpha_1$ (nickel filter), divergence slit 1°, medium resolution soller, detector slit 0.05° ($\approx 0.006''$), scan rate 0.2° 2 θ /min, chart abscissa 1 in. = 1° 2 θ , time constant 8 s. Proportions of LiF and olivine powders were adjusted to produce nearly equivalent intensities of the olivine 062 and LiF 220 reflections. Smear mounts in a non-rotating sample holder were adjusted so that their surfaces coincided with

the rotation axis of the goniometer. Each mount was oscillated four times across the range $62-66^\circ 2\theta$; the resultant two up- and down-scan pairs were averaged for three mounts of each olivine sample, and the average and standard deviation for all 6 pairs then calculated. Values of 2θ were measured by locating half-peak widths with a steel scribe and micro-rule under a binocular. Diffractometer scan rate and chart drive speed were closely checked. The 2θ

TABLE I. *Chemical analyses and 062 diffraction characteristics of olivine concentrates, eastern Azores*

No.	Weight % oxides*					Totals†	Olivine end-members (mole %)					$\Delta 2\theta \ddagger$	σ
	FeO	MgO	CaO	MnO	NiO		Fo	Fa	Teph.	Ni-Ol	Larn.		
S. TIP	11.93	48.11	0.51	0.17	0.21	102.10	86.88	12.09	0.17	0.20	0.66	2.944 ^o	0.005
925	14.02	44.87	0.56	0.26	0.22	99.72	84.03	14.73	0.27	0.22	0.75	2.952	0.017
SMA	14.20	44.73	0.57	0.20	0.19	99.65	83.89	14.94	0.21	0.19	0.76	2.949	0.003
100	14.28	45.94	0.38	0.20	0.18	101.50	84.40	14.71	0.21	0.18	0.50	2.975	0.015
926	14.31	44.93	0.45	0.22	0.18	99.95	83.98	15.00	0.23	0.18	0.60	2.987	0.020
6A	14.34	45.91	0.42	0.21	0.21	101.70	84.27	14.76	0.21	0.21	0.55	2.965	0.010
281A	15.07	45.54	0.28	0.22	0.24	101.90	83.64	15.53	0.23	0.24	0.36	2.998	0.014
181A	15.23	45.34	0.19	0.22	0.28	101.70	83.51	15.73	0.23	0.27	0.25	2.975	0.020
12A	15.68	44.55	0.47	0.24	0.21	101.40	82.61	16.31	0.25	0.21	0.62	3.000	0.020
904	15.82	43.83	0.38	0.23	0.25	100.19	82.33	16.67	0.24	0.25	0.51	3.001 [§]	
214A	16.08	42.97	0.46	0.26	0.19	99.14	81.74	17.16	0.28	0.19	0.63	3.034	0.010
212A	17.25	43.52	0.41	0.29	0.23	101.80	80.93	17.99	0.30	0.22	0.58	3.019	0.014
7A	17.39	42.32	0.38	0.22	0.25	99.74	80.45	18.55	0.24	0.25	0.51	2.987	0.017
83A	17.66	42.80	0.27	0.26	0.20	100.80	80.52	18.64	0.27	0.19	0.36	3.007	0.014
10A	17.78	42.63	0.31	0.24	0.19	100.70	80.35	18.80	0.25	0.19	0.42	2.984	0.017
912	20.18	40.03	0.53	0.29	0.16	99.92	77.02	21.78	0.31	0.16	0.73	3.119	0.020
104A	25.94	34.02	0.80	0.43	0.09	98.13	68.82	29.44	0.49	0.10	1.16	3.151	0.026

* Atomic absorption analyses. Duplicate analyses for Mg and Fe (see text).

† Calculated for R_2SiO_4 .

‡ $220(\text{LiF})-062(\text{OI})$; average of 12 diffractometer scans (increasing and decreasing 2θ directions) according to method of Jackson (1960). Cu-K α

§ Insufficient material for replicate mounts.

Locations of samples

S. TIP Southernmost exposure, beacon rock, Formigas Shoals.
 925 Basalt flow exposed on southern shore road 250 m north of Feteiras, São Miguel Island.
 SMA Basalt flow from quarry above coquina zone 1 km north-west of Praia, Santa Maria Island.
 100 Ankaramitic flow at Ponta do Arnel, eastern São Miguel.
 926 Olivine nodule from basalt dike exposed on cliffs south-west of airport, Santa Maria.
 6A Scoria cone exposed along shore 20 m south of lighthouse at Ponta do Arnel, São Miguel.

281A Basalt flow, road cut above Algarvia, north shore of São Miguel.
 181A Basalt flow near Pedreira, eastern São Miguel.
 12A Uppermost flow of sequence of analysed flows overlying the scoria cone (sample 6A). Sample obtained at approximately 8 m above sea level.
 904 Xenocryst in latite flow, east wall of Ribeira do Guilherme. Approximately 1 km north of village of Nordeste, São Miguel.
 214A Basalt flow underlying latite at Lomba da Cruz, eastern São Miguel.
 212A Ankaramitic flow north of village of Fazenda, eastern São Miguel.
 7A Same locality as sample 12A, approximately 2 m above sea level.
 83A Ankaramitic flow north of Outeiro Alto bench mark (649), new Tronqueira road, 500 m elevation.
 10A Same locality as sample 12A. Sample obtained at approximately 6 m above sea level.
 912 Basalt exposed near 308-m bench mark north-west of Pedreira, eastern São Miguel.
 104A Basalt dike exposed in the Ribeira do Guilherme at an elevation of 285 m, eastern São Miguel.

locations of Herkimer quartz d_{211} , d_{212} , and d_{203} were used to check diffractometer alignment in the range $60-70^\circ 2\theta$. Deviation from calculated values increased 0.003° over the range $62-66^\circ$; the observed 2θ values were corrected proportionately.

For inter-laboratory comparison we obtained, through the kindness of K. J. Murata, a sample of his analysed olivine ML-2 (Murata *et al.*, 1965) for which he reported a $\Delta 2\theta$ value of 2.929, $\sigma = 0.0031$. We obtained 2.908, $\sigma = 0.0141$, in our laboratory. Recently Fernandez, using the same smear mounts, obtained 2.905, $\sigma = 0.0140$, on a diffractometer in the Kline

Laboratories.¹ The determinations of 2.929 and 2.908 do not overlap within the ranges of one standard deviation calculated by us and by Murata. There thus seem to be slight differences in the compositions of the 'reagent grade' LiF used. On noting our findings with regard to inequalities in LiF, Dr. Murata suggested that inter-laboratory comparison of olivine 062 behaviour could be established by using the U.S. Geological Survey dunite standard, DTS-1 (Flanagan, 1967, 1969), as a reference. DTS-1 gives a very sharp olivine 062 reflection, and Murata (written communication, 1969) reports a $\Delta 2\theta$ ($220_{\text{LiF}} - 062_{\text{olivine}}$) separation of 2.820 ± 0.004 . We obtain a $\Delta 2\theta$ value of 2.800, $\sigma = 0.0054$. The interlaboratory difference is the same as noted above for ML-2. For direct comparison with previous studies, we therefore have added 0.020° to our $\Delta 2\theta$ values.

The advantages of the 062 method in our experience outweigh the disadvantages that might arise in its application to the petrologic study of olivine-bearing systems. In contrast with the use of d_{130} , the method has the advantage of higher sensitivity owing to greater dispersion achieved at higher 2θ angles. (Across a given compositional range, d_{130} varies more than 1.5 times that of d_{062} , but in angular divergence the variation is less than half the change in 2θ of 062.) The $K\alpha$ doublet, though less intense, is well resolved under the specified operating conditions, and the effects of zoning or of multiple compositions can be more easily observed. One disadvantage is possibility of interference from other minerals if the olivines have not been carefully separated: d_{060} ($I/I_0 \simeq 6$) of Cr,Al-bearing diopside-sahlites in Azores ankaramites has nearly the same range of values as d_{062} of olivine in the range Fo₈₀₋₉₀. The intense Fe-rich spinel 440 reflection can interfere over the entire Fo-Fa range. Pure chromite does not interfere, but Cr-bearing magnetite, such as that with $\sim 18\%$ Cr₂O₃ occurring in the groundmasses of many Azores volcanics, could interfere in the high-Mg olivine range.

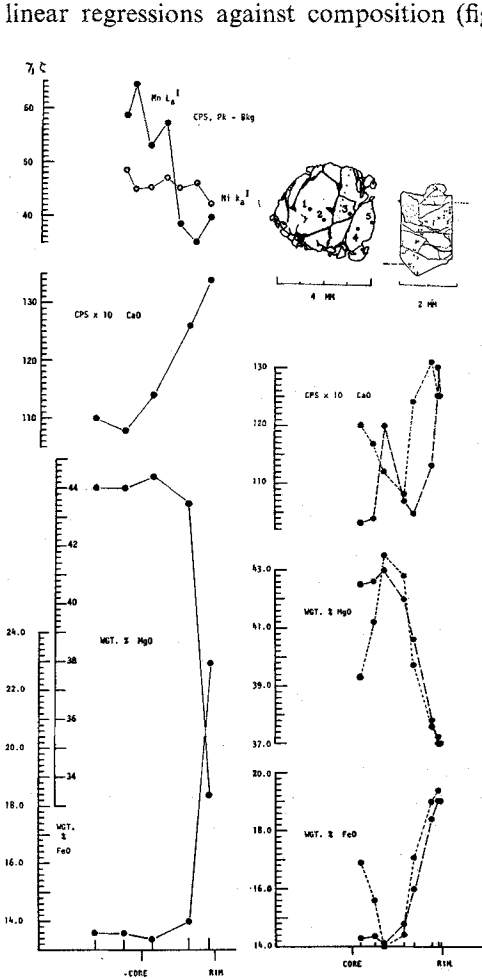
The choice of Cu radiation in the earlier 062 regression studies was probably made because of its widespread availability. This might appear inappropriate for diffraction study of olivines because of the marked change in absorption coefficients vs. composition in zoned crystals or mixtures. It is concluded from the discussion below, however, that the use of Cu radiation contributes to, rather than detracts from the versatility of the method.

Discussion

The spread in the X-ray data is attributed to mixtures of different generations of olivines in some of the flows, and to variations in zoning. Both types of heterogeneity can be regarded as mixtures of homogeneous olivines of different composition, each of which possesses its own uniform cell dimensions. These mixtures of slightly different Mg-Fe solid solutions cause spurious deviation in regression of 2θ angles against bulk composition. Examining this behaviour more closely may provide a rationale for comparing the anomalous results with the 'normal' regression of the five most homogeneous samples.

Figs. 2 and 3 illustrate results of electron-probe multiple-point analyses across two zoned phenocrysts of different bulk composition from the Nordeste complex. They are considered to be typical of the more strongly zoned olivines. The cores of both are close to Fo₈₅, but their bulk compositional differences result from different gradients of normal zoning. The shallower gradient (fig. 3) shows up as greater line broadening in diffractometer tracings (fig. 4) and in greater departure from 'normal'

¹ This standard deviation is representative of our runs (table 1); it also agrees closely with the 'between chart' σ (0.0156) obtained by Chayes and MacKenzie (1957) under similar experimental conditions.



FIGS. 2 and 3: Fig. 2 (left, and left crystal). Electron-probe microanalysis of zoned phenocryst in ankarinite (no. 100 in table I). Mn and Ni were analysed at points (unnumbered) along traverse indicated in sketch. Scales in this figure and in fig. 3 are equivalent. Fig. 3 (right and right crystal). Electron-probe microanalysis of zoned phenocryst in olivine trachybasalt (no. 10A). The two radial traverses are indicated by short- and long-dashed lines.

linear regressions against composition (fig. 5). The composite peak representing a given d_{hkl} in compositionally different volumes of olivine thus cannot provide, by way of inference from a regression line, the mean chemical value. The shift in 2θ may become significant in Mg-Fe solid solutions for which small changes of 2θ relate to concentrations of other elements in addition to Mg and Fe.

The origin of the anomalous 2θ shift can be accounted for in principle, and assessed qualitatively. Part of the explanation lies in the effect on intensity produced by change in mass absorption coefficient, μ/ρ , which is of large magnitude for Cu- $K\alpha$ in olivines. In assessing intensity change vs. composition in model calculations, however (we used a broad Gaussian weight-distribution across a 10% Fo-Fa interval employing the well-known relation $I_x = I_0 e^{-(\mu/\rho)\rho x}$), we found that the skewing of the 062 peak was only $0.006^\circ 2\theta$. This equates to a bulk compositional change toward more magnesian olivine of 0.3 wt %, only a fourth of the average observed error for many of the anomalous plots¹ in fig. 5. The model assumed ideal diffraction of the $K\alpha_1$ line, the composite of which is not overlapped by the $K\alpha_2$ composite. But in fact overlap occurs (fig. 4), and $K\alpha_2$ radiation diffracted from Fe-richer portions of the mixture occurs on the high- 2θ side of the $K\alpha_1$ composite peak; integration of intensities caused by the overlap further skews the composite $K\alpha_1$ peak to higher values of 2θ , i.e., in the direction of

more Mg-rich olivine. The anomalous $\Delta 2\theta$ shift will further depend on asymmetry

¹ The close correspondence between atomic absorption analyses and electron-probe values (table II) refutes major compositional error arising from analysis of Fe, Mg, and Ca in phases other than olivine, which might inadvertently have been present in the concentrates. We estimated < 0.1% impurities from microscopic examination; EBS images of crystals indicated that submicroscopic

or polymodal distribution in gradients of weight fractions vs. composition. The broader the frequency distribution, the lower will be the resulting slope for linear regression of 2θ values against bulk composition, as compared to that for samples that are internally more homogeneous.

Thus in relating four of our five most homogeneous zoned olivine samples to the Hawaiian regression line 'H' (fig. 5), inferred compositions are obtained that are more forsteritic than the mean chemical values. If the height/width ratio of the 062 peak of Murata's sample ML-2, examined by us, is representative of all his analysed olivines, they were very likely more homogeneous and less zoned than any of our phenocrystic samples from the Nordeste complex.

Compositional and 062-related parameters of least-zoned Azores olivines. Microprobe analyses across several crystals in each of the four most homogeneous samples closely bracket the FeO and MgO percentages of the analysed concentrates (tables I and II). MgO percentages correspond more closely than those for FeO, in comparing microprobe and atomic absorption results (sample 281A is an exception). Where CaO determined by electron-probe microanalysis is lower than found by atomic absorption, calculated totals of olivine end-members are also low. (Olivines used as microprobe standards are listed in table II.) Inasmuch as inter- and intra-crystal variations in calcium have not been thoroughly studied in the Balsam Gap forsterite and Crestmore monticellite standards, we believe the atomic absorption values more nearly reflect the bulk CaO contents of the Azores olivine samples.

The 062 diffraction peaks of four of these samples are compared in fig. 4 with others representing strongly zoned crystals and mixtures of multiple generations of phenocrystic olivines in the same rock. Ranges of height/width ratios of the $K\alpha_1$ peaks reflect a close correspondence between X-ray peak quality and narrowness of compositional range in a given sample.

The regression of diffraction data for the four least-zoned olivine samples and one compositionally bimodal mixture, calculated in relation to FeO (fig. 5), lies below the regression line for Hawaiian olivines, but both lines are within the range of σ (± 0.0151 av.) of our determinations. The difference between the lines represents the residual after correcting for the difference in LiF behaviour discussed previously (p. 169). The Azores line represents the linear equation

$$\Delta 2\theta = 2.6672^\circ + 0.0225 \text{ FeO wt } \%. \quad (1)$$

The variation of MnO with FeO is identical to the Hawaiian trend. The Azorean and Hawaiian trends for CaO are quite different, but values overlap in the range of 13.5-16.5 wt % FeO. It is doubtful if nickel or cobalt could contribute significantly to the difference between the two volcanic regression lines.

The X-ray behaviour of 104A (fig. 5), as compared to the more Fe-rich Hawaiian samples, suggests that further study should be made of high-calcium olivines. Excluding major error in FeO determination, the amount of CaO in 104A (analysed by oxide inclusions are rare. If clinopyroxene contamination were responsible for creating low $\Delta 2\theta$ values, then these should be matched by high CaO percentages. The analytical data (table I) effectively rule out this possibility.

microprobe) should place $\Delta 2\theta$ for this sample much nearer the range of the volcanic regression lines, even if the crystals in this sample are strongly zoned. Inasmuch as lattice constants may vary non-linearly with substitution if ordering is involved, the question arises as to whether Ca in high-Ca olivines is ordered in the M_2 sites at solidus temperatures, causing d_{062} to be smaller than predicted from a linear relationship. If ordering is involved, we would expect the threshold Ca concentration for

TABLE II. ΔFeO compared to X-ray diffraction peak characteristics in Azores olivines used for $\Delta 2\theta$ regression determinations

No.	Electron-probe analyses*		Atomic absorption FeO analyses†	Height/width ratio, Olivine 062 $K\alpha_1$	Comments
	FeO wt. %	ΔFeO			
S.TIP	11.63-12.04	0.41	11.93	8.25	Slight detectable zoning; minor compositional differences between grains.
926	14.57-14.96	0.42	14.31	9.05	
281A	14.77-20.92	6.15	15.07	6.50	
214A	13.55-13.98	(a) $\Delta_a = 0.43$	16.08	4.80	Moderate zoning; minor compositional differences between grains. Bimodal compositional range in rock; (a) zoning minimal; (b) zoning prevalent in this compositional range.
		$\Delta_{total} = 8.11$			
		(b) $\Delta_b = 1.40$			
912	19.75-22.25	2.50	20.18	6.75	Detectable zoning; minor compositional differences between grains.

* Standards in Yale Collection used for the electron-probe microanalyses:

Forsterite (Balsam Gap, N.C.) Total Fe as FeO 7.28 % E. G. Zies, analyst, Geophysical Laboratory;

Olivine T (forsterite) FeO 7.2 % (total Fe as FeO) (Smith and Stenstrom, 1965);

Hortonolite (obtained from J. V. Smith) FeO 44.15 % (total Fe as FeO);

Monticellite (Crestmore, California) FeO 3.78 % (Moehlman and Gonyer, 1934) U.S.N.M. no. 96552.

† Data from table I.

ordering to increase with increasing fayalite content. Birle *et al.* (1968) suggested that the approximately close-packed structure of olivine inhibits cation exchange between M_1 and M_2 sites. But for olivines with CaO in the 0.5-1.0 % range of minimum concentration, ordering of Ca may be a reasonable possibility.

Regression of $\Delta 2\theta$ ($220_{LiF} - 062_{Olivine}$) against Fo mole % for the Azores olivines is compared below with the 'plutonic' and Hawaiian volcanic lines. The equations for each are:

$$\Delta 2\theta = 4.5644^\circ - 0.018834 \text{ Fo mol \% (Murata } et al., 1965), \quad (2)$$

$$\Delta 2\theta = 4.5049^\circ - 0.018009 \text{ Fo mol \% this study,} \quad (3)$$

$$\Delta 2\theta = 4.4722^\circ - 0.018015 \text{ Fo mol \% (Hotz and Jackson, 1963).} \quad (4)$$

The Azorean and Hawaiian regression equations (3 and 2 respectively) are distinguishable chiefly because the slopes (note tangent values) of the Azorean and *plutonic* equations are nearly equivalent. The lesser slope and higher $\Delta 2\theta$ intercept of equation (3), as compared to (2), reflect the higher CaO percentages in those Azorean olivines of higher Fo content, in contrast to the Hawaiian phenocrystic olivines in the same Fo–Fa range. The over-all separation of the two regression lines across the Fo–Fa range they cover, however, is not statistically significant, as the 95 % confidence intervals about $Fo_{84 \pm 2}$ of each line overlap strongly.

Despite the ‘volcanic’ character of both the Azores regression equations the cores of large, zoned phenocrysts may possibly record an early plutonic equilibration that was not subsequently destroyed. This possibility might be investigated by determining partition coefficients of minor elements in the *cores* of coexisting ferromagnesian phenocrysts and comparing them to known temperature- (and pressure-) dependencies. Ni-fractionation studies (Häkli and Wright, 1967), as extended experimentally to higher pressures, might prove rewarding in this respect.

Crystallization trends. The over-all trend of crystallization of the olivines is one of iron enrichment, but no simple correlation can be made with sequence of extrusion. Some of this behaviour can be explained by incorporation of batches of cumulus crystals in the eruption of successively differentiated liquids. An extreme example is the composition of xenocrystic olivine in latite (904), which lies in the same range of composition as the olivines in basalts and trachybasalts.

Trends of Fe, Mg, and Ca in the bulk olivine samples of the Nordeste Complex are quite faithfully reflected in the pattern of element zonation in the two phenocrystic olivines for which multiple-point electron-probe analyses were made (figs. 2 and 3).¹ The single profile for NiO (fig. 2) reflects the dominant trend of decreasing Ni as Fe increases, and is in agreement with the electron-probe scans of Forbes and Banno (1966).

¹ We also examined the same crystals using electron back-scattering in an attempt to detect submicroscopic Cr concentrations. Concentrations were noted only near the rims of crystals. Spot analysis on Fe-rich spinels in the mesostasis surrounding the crystals reveal up to 18 wt % of Cr_2O_3 . We conclude that Cr does not reside in the lattice of these crystals in quantities detectable by electron-probe microanalysis, although Brown (1967) suggested that minor quantities may be incorporated at high temperatures.

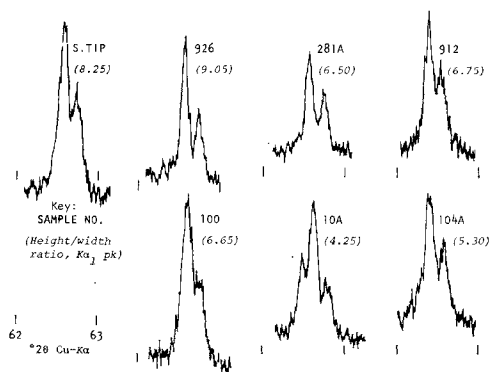


FIG. 4. Contrasts in X-ray diffraction peak quality as related to degree of zoning in phenocrystic olivines. Greater height/width ratios (upper row) represent least-zoned, homogeneous samples (table II). Compare peak broadening with zoning gradients in samples 100 and 10A (figs. 2 and 3).

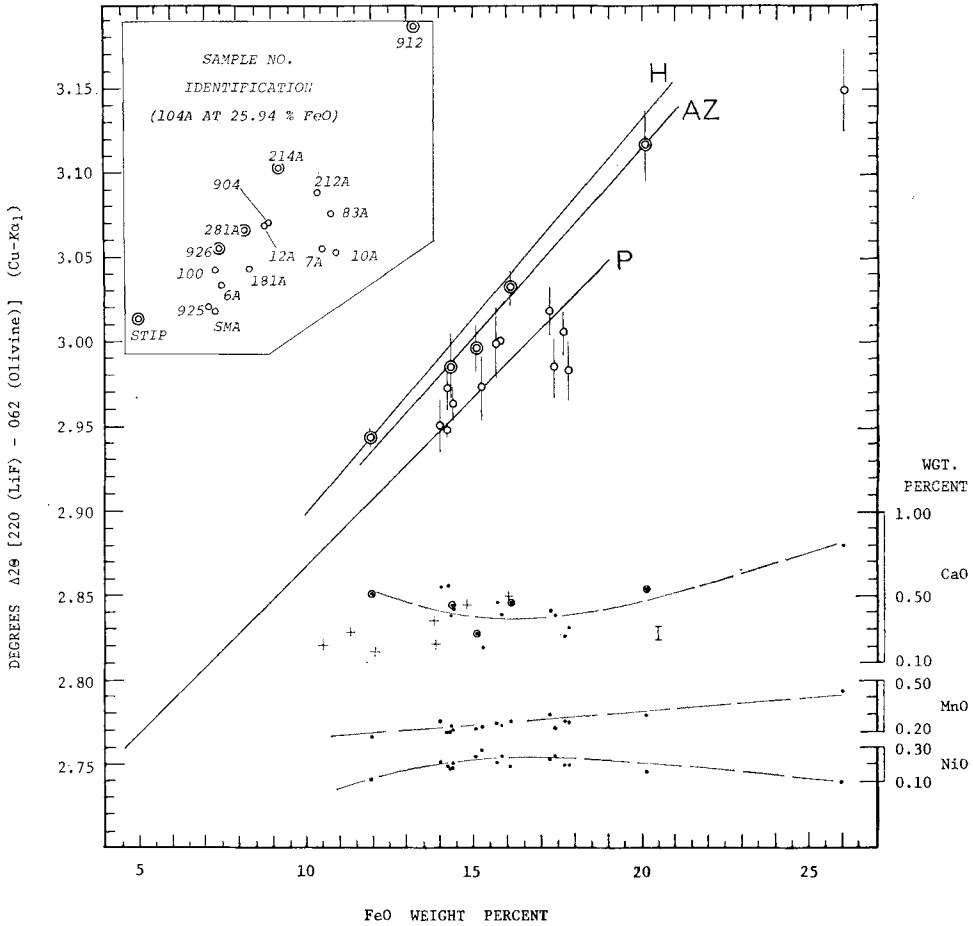


FIG. 5. X-ray diffraction characteristics of Azores olivines as related to zoning (see text and preceding figures) and concentrations of major and 'minor' elements in bulk analyses of olivine concentrates. Regression line (AZ) based on least-zoned olivines (double circles). Vertical bars give standard deviation of error, with all error assumed concentrated in $\Delta 2\theta$. CaO values for Hawaiian olivines (Murata *et al.*, 1965) are shown as crosses and variation-bar. Minor element trends discussed in text. Hawaiian (H) and plutonic (P) regression lines from Murata *et al.* (1965) and Hotz and Jackson (1963), as recast to FeO by Murata (1965).

Calcium decreases with increasing iron content of olivine from $Fe_{0.87}$ to $Fe_{0.80}$ mol %, then begins to increase with further increase of fayalite content. Referring to the oppositely curved trends of CaO and NiO in fig. 5, the correlation coefficient of $(CaO + NiO)$ vs. FeO, 0.7074 (-0.7838 with respect to mol % Fe), reflects a coincidence of contemporaneous but independent magmatic processes. The NiO percentage in the most magnesian phenocryst sample (from the Formigas Shoals) is less than in phenocrysts from São Miguel, or in nodular olivine from Santa Maria, all of which are more Fe-rich (table I; fig. 5). An increasing trend of NiO with FeO in the 9–13 %

FeO range also appears in the analyses of New Zealand nodular olivines reported by Rodgers and Brothers (1969).¹ These apparently increasing trends of NiO in two widely different petrologic provinces suggest that the fractionation behaviour of Ni in Mg-rich olivines may not always define a negative slope with respect to increasing FeO. The trend for early-formed olivines may define a positive slope while olivine precipitates as the only mafic silicate phase under uniformly low partial pressures of oxygen and sulphur. Once joined by pyroxene, however, NiO concentration in olivines should then define a negative slope when plotted against FeO, as White's data (1966, fig. 13) seem to bear out.

The minimum in the curve for CaO (fig. 5) nearly coincides with the maximum for NiO. But comparison of CaO in olivine with host-rock normative anorthite (fig. 6) suggests that CaO in the olivine concentrates is controlled in part by cotectic crystallization of plagioclase (plotting $\text{CaO}_{\text{olivine}}$ vs. $\text{CaO}_{\text{total rock}}$ shows no definable trend). The data, all from the Nordeste complex, indicate that the incorporation of Ca in olivine is adversely affected by higher normative anorthite content in the host rock. Olivines richer in Fe (fig. 5) suggest that the trend was reversed with further iron enrichment, either caused or accentuated by concomitant depletion of anorthite component from the melt during plagioclase fractionation. More information from both alkalic and tholeiitic sequences is needed to further test this hypothesis.

A possible extension of the 'anorthite effect' arises from noting a difference in Azorean and Hawaiian olivine CaO trends: the Azorean trend (fig. 5) defines a curve with a minimum in the 15–17% FeO range, whereas it appears the Hawaiian trend attains a maximum in the same range of FeO. If entry of Ca in olivine at solidus temperatures is partly or largely controlled by the tenor of anorthite in cotectic plagioclase, as suggested above, then we would infer that calcic plagioclase began co-precipitating with olivine at an earlier stage of its iron enrichment in the Hawaiian magmas than occurred in the Nordeste alkali basaltic sequence in the Azores.

Differences in the average chemistries and petrographic features of basaltic rocks allow us to predict that this should happen. Manson (1967, table 16) records higher average normative anorthite in olivine tholeiite basalts than in alkali olivine basalts. He further records approximately 10% higher average An-content in normative plagioclase in olivine tholeiites, even though the total range of An-content reported

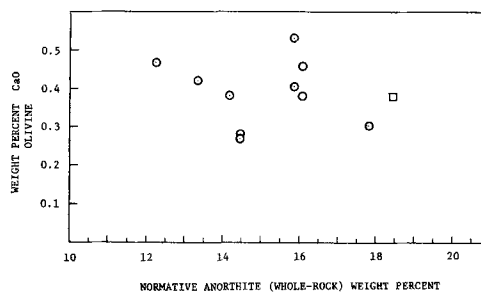


FIG. 6. Variation of CaO in phenocrystic olivines with normative anorthite of analysed host-rocks. Square symbol: xenocrystic olivine in latite flow (no. 904). All are from the Nordeste basaltic complex, São Miguel Island.

¹ Alternatively, if the Ni concentrations in the Formigas basalts were lower relative to the other Azorean basalts we should expect according to the distribution law that this would be reflected in lower Ni concentration in the phenocrystic olivine.

in both rock-types is about the same (Manson, 1967, table 16 and fig. 9). Yagi (1967) concluded that experiments on natural basalts suggest that all basalt liquids begin crystallization in the olivine primary phase volume, but Wilkinson (1967) suggests that olivine is less abundant and plagioclase perhaps more abundant as phenocrystic phases in basalts of tholeiitic affinity than in alkali olivine basalts. We therefore conclude from these observations that plagioclase crystallization should begin to manifest itself in terms of entry of Ca into olivine at earlier stages of olivine fractionation in tholeiitic basalts because the compositions of tholeiites lie closer to the plagioclase field boundary. As cotectic fractionation of both phases continues, more Ca will enter olivine passively as the anorthite content of plagioclase decreases. Except for Murata's sample HA-1, the petrogenic scheme here proposed might explain the positive slope of CaO vs. FeO for the Hawaiian samples in the same range of FeO in which the Azores samples define a negative slope. The change to a positive slope in the Azores olivine trend was 'delayed' to later stages of iron-enrichment because precipitation and fractionation of calcic plagioclase began at a later stage. The same paragenesis can be inferred from the zonal gradient of CaO in the phenocryst from trachybasalt (fig. 3). The shallow Mg-Fe gradients in the central part of the crystal from an ankaramite (fig. 2), on the other hand, may record a partly xenocrystic history. Porphyritic feldspar basalts and trachybasalts are the exception rather than the rule in the Nordeste complex, and phyric feldspars are rare in other phenocrystic olivine basalts sampled elsewhere in the eastern Azores.

Conclusions

The forsterite contents of the most magnesian olivines in alkali olivine basalts and ankaramites from the eastern Azores do not differ significantly from those in volcanics of tholeiitic affinity. Both, in turn, overlap the range of Fo-content of olivines in nodules and xenoliths of inferred mantle origin (Brown, 1967, table 3) but are not nearly as magnesian as olivines in Hawaiian lherzolite inclusions (White, 1966). The most forsteritic olivines from the eastern Azores are not as rich in Ni as Hawaiian and Antarctic xenolithic and phenocrystic olivines (White, 1966; Forbes and Banno, 1966, respectively), nor are they as Ni-rich as northern Mid-Atlantic Ridge xenolithic olivines analysed by Muir and Tilley (1964). The relatively high CaO values that accompany the values for nickel in the Azores samples are typical of volcanic olivines. Neither the bulk compositional features of the more forsteritic olivines nor the zonal gradients suggest that the eastern Azores phenocrysts began crystallizing at sub-crustal depths.

The 062 diffraction characteristics of the phenocrystic olivines are shown to be strongly affected by pronounced zonal gradients of Mg and Fe, and can yield anomalously high Fo-values from the X-ray regression curve. Least-zoned phenocrystic olivines and one sample from an olivine nodule, however, have $\Delta 2\theta$ ($220_{\text{LiF}} - 062_{\text{olivine}}$) characteristics similar to the Hawaiian olivines studied by Murata *et al.* (1965), in which the tenor of larnite exerts a prominent control.

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APPENDIX

As a test of the role of 'minor' elements in affecting the olivine 062 spacing, the equations for b_{adjusted} and c_{adjusted} (Louisnathan and Smith, 1968, p. 1131) were combined to obtain an equivalent expression for d_{062} . Since b and c cannot be calculated directly from this single physical parameter, an approximation was made by fixing the sine and cosine functions of χ ,

{062} \wedge {001}, arbitrarily as constants because of their slight variations between the forsterite and fayalite end-members:

$$\sin \chi = 0.86935 \text{ (Fo) to } 0.86813 \text{ (Fa), mean } 0.86874;$$

$$\cos \chi = 0.49419 \text{ (Fo) to } 0.49635 \text{ (Fa), mean } 0.49527.$$

Therefore the relation $d_{062_{\text{obs}}} = 0.0834 b_{\text{obs}} \sin \chi + 0.25 c_{\text{obs}} \cos \chi$,

combined with Louisnathan and Smith's constants for tephroite (Mn) and larnite (Ca), gives

$$d_{062_{\text{adj}}} = d_{062_{\text{obs}}} - 0.02504 \text{ Mn} - 0.18678 \text{ Ca}. \quad (5)$$

Adding mole-fractions of Ni-olivine to the above values, an iterative programme was used to increase the correlation coefficient between $d_{062_{\text{adj}}}$ and Fo (mol %), taking the five samples for the previous $\Delta 2\theta$ regression calculations. The resulting constant for Ni-olivine is -0.10475 .

In so far as the Mn and Ni constants are overshadowed by the product of mole-fraction of larnite multiplied by the Ca constant, the use of this equation can act as an independent check on the precision of calcium analyses of olivines.

Observed and adjusted d_{062} values for the five least-zoned olivine concentrates are plotted in fig. 7. The adjusted d -values closely approach linearity after subtracting the effects of Ca, Mn, and Ni. The resulting line of best fit is parallel to, and lies $\sim 0.0005 \text{ \AA}$ above the line for d_{062} based on the extrapolated b and c cell dimensions of pure forsterite and fayalite (Louisnathan and Smith, 1968, p. 1130,

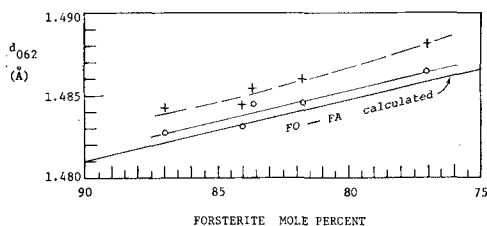


FIG. 7. Observed (crosses) and adjusted (circles) d_{062} values for the least-zoned olivines used in establishing the regression line in fig. 5. Line calculated for pure Fo-Fa solid solutions based on Louisnathan and Smith's extrapolated b and c cell dimensions (1968, p. 1130, table II).

table II). Using Louisnathan and Smith's equations (4) and (6) (1968, p. 1129) to calculate 'observed' d_{062} from our compositions for these olivines (table I), the calculated d -values are lower than the observed, by $\sim 0.001 \text{ \AA}$, sample 926 excepted. The data are compared in table III.

TABLE III. Comparison of d_{062} observed, calculated, and adjusted for the least-zoned Azores olivine samples

Sample	Observed	Calculated*	Adjusted†	
			[-(Mn, Ca) only]	[-(Mn, Ca, Ni)]
S. TIP	1.4843 Å	1.4832 \pm 0.0007 Å	1.4830 Å	1.4828 Å
926	1.4844	1.4842	1.4833	1.4831
281A	1.4856	1.4841	1.4849	1.4847
214A	1.4860	1.4851	1.4848	1.4846
912	1.4881	1.4870	1.4867	1.4865

* Our compositions (table I) applied to Louisnathan and Smith's equations (4) and (6) (1968).

† Equations (5), and (5) with constant for Ni added; this study.