

Structure refinements of seven natural olivine crystals and the influence of the oxygen partial pressure on the cation distribution

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Abstract. Mg/Fe order in olivine has been determined by X-ray diffraction data, for example by Wenk and Raymond (1973). We have now studied the dependence of the Mg/Fe order vs. oxygen partial pressure. Two natural olivine samples of volcanic origin containing respectively 10 and 12 % fayalite were selected. The atomic positions, anisotropic temperature factors, extinction coefficient and site occupancies have been refined to R -values of 2.2%. In total seven crystals were studied and the distribution coefficients K_D determined. A significant change in the Mg/Fe order could be detected after subjecting five of the crystals to well defined oxygen partial pressure conditions of 10^{-16} and 10^{-21} bar. An increase of K_D from 1.09 and 1.06 (natural) to 1.20 under low pO_2 conditions could be observed. This means higher order for Fe in $M1$. A decrease to $K_D = 0.80$ was found under high pO_2 conditions, meaning higher order for Fe in $M2$.

These experiments seem to indicate that the prevailing oxygen partial pressure determines the different Mg/Fe order found in natural olivine crystals.

1. Introduction

The basic structure of olivines (Bragg and Brown, 1926) is a close packing of oxygen with Mg and Fe occupying one half of the distorted octahedral interstices, known as $M1$ and $M2$ sites, and Si occupying one-eighths of the tetrahedral interstices (Fig. 1). Several structures of olivines of different compositions have been refined from X-ray data with emphasis on structural variations. In recent years this interest has been concentrated on the determination of the Mg/Fe solid solution series. Earlier work on isostructural compounds like monticellite $CaMgSiO_4$ (Onken, 1965) and glauchroite $CaMnSiO_4$ (Caron et al., 1965) has shown that the cations are ordered in

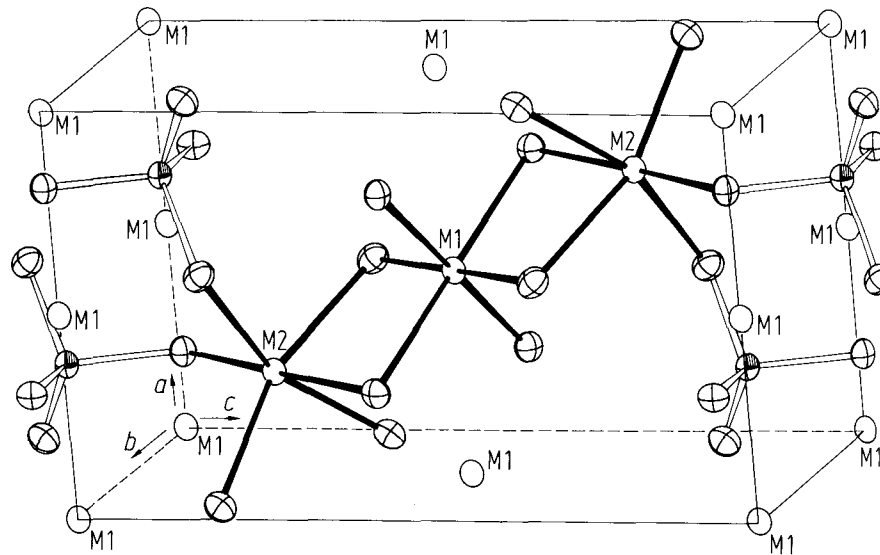


Fig. 1. An ORTEP drawing of the crystal structure of olivine

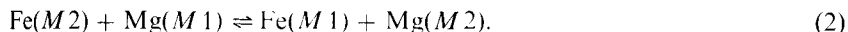
these crystals and this has stimulated researchers to look for ordering also in olivines.

For the Fe–Mn- and Mg–Mn-olivines (Brown, 1970; Huggins, 1973) and Ni–Mg-olivines (Rajamani, Brown and Prewitt, 1975) cation ordering derived from X-ray diffraction is in agreement with cation distributions predicted by Burns (1970). For the Mg–Fe olivines however the problem of cation ordering in the two distinct octahedral sites $M1$ (point symmetry $C_i-\bar{1}$) and $M2$ (point symmetry C_s-m) has become a controversial subject in the last years.

Partial order was first derived from spectroscopic measurements (Burns, 1970; Bush et al., 1970) but the results were not conclusive (Burns, 1970). The latest development of X-ray single crystal diffractometers has greatly improved the quality of the measured X-ray data and thus improved the resolution of such crystal structure refinements. It is possible today to determine electron densities in fraction of an electron. The Mg/Fe distribution and the cation ordering has been measured in several Mg–Fe olivines and in these investigations different degrees of ordering were detected in different crystals. It was not possible, however, to find a correlation between the ordering parameter and thermodynamic parameters, like for example the temperature. For the purpose of describing the cation ordering over the positions $M1$ and $M2$ we define a distribution coefficient

$$K_D = \frac{\text{Mg}_2 \cdot \text{Fe}_1}{\text{Mg}_1 \cdot \text{Fe}_2} \quad (1)$$

Mg2 stands for Mg on $M2$ etc. K_D is related to the exchange reaction



Finger (1970) and Finger and Virgo (1971) studied a volcanic olivine crystal from Australia, and a lunar olivine crystal from rock 10020, both of which are believed to have rapid cooling histories. Both samples were reported to show a preference of Fe for the smaller $M1$ site (see also the data points in Fig. 5). In contrast Wenk and Raymond (1973) in a similar study report a preference of Fe for $M2$ in a metamorphic crystal with about 9 mol% fayalite. Brown (1973), in another study describes small order, which he thinks is insignificant. In his high temperature experiments he finds an increasing distortion of the $M1$ site with increasing temperature. Using electron spin resonance techniques Chatlein and Weeks (1973) have found Fe^{3+} exclusively at the $M1$ position, on the other hand Zeira and Hafner (1973) found statistical distribution of Fe^{3+} between the $M1$ and $M2$ sites.

The results accumulated so far, do not lead to an unambiguous picture for Mg/Fe ordering in olivines and no underlying principle has been proposed to explain the results. Obviously there is no convincing correlation of K_D , the distribution coefficient, to the composition; and the quite different cooling histories of the crystals tend to have only minor influence on the Mg–Fe ordering.

From measurements of the electrical conductivity of olivines (Will, Cemic, Hinze, Seifert and Voigt, 1979) we have found that the prevailing oxygen partial pressure is influencing greatly the physical properties of these crystals. We have therefore started to explore also the influence of the oxygen partial pressure on the crystal structure of olivines, especially on the cation ordering. This parameter has up to now been neglected. It is our suggestion that the oxygen partial pressure is the significant driving force for the cation ordering on the $M1/M2$ sites in olivines, and we believe we can demonstrate a correlation between the cation distribution and the prevailing oxygen partial pressure.

Our interest has been concentrated on olivines of volcanic origin and we have chosen for our studies natural crystals from the Dreiser Weiher, a quarternary Maar-volcano of the West Eifel, Federal Republic of Germany. In this locality olivines of different compositions are found in ultramafitic nodules, which have reliable analytical data and indications about the cooling histories available (Frechen, 1963; Vieten, 1973).

In this paper we wish to report the results of several refinements of the structures of differently treated crystals taken from two olivine samples collected at the Dreiser Weiher. The samples are labelled *FE10* and *FE12* referring to their fayalite content of 10 mol% Fa and 12 mol% Fa respectively. The results of wet chemical and microprobe analysis are listed in Table 1. From this analysis we calculate the actual compositions of

Table 1. Analytical data (weight %) of the two olivine samples *FE 10* and *FE 12*

| | <i>FE 10</i> | <i>FE 12</i> | Mol % | <i>FE 10</i> | <i>FE 12</i> |
|--|--------------|--------------|----------------------------------|--------------|--------------|
| SiO ₂ | 39.48 | 40.29 | Mg ₂ SiO ₄ | 88.50 | 86.00 |
| MgO | 48.70 | 46.62 | Fe ₂ SiO ₄ | 10.72 | 12.60 |
| FeO | 10.51 | 12.18 | | | |
| Fe ₂ O ₃ | 0.14 | 0.69 | | | |
| NiO | 0.31 | 0.28 | | | |
| CaO | 0.33 | 0.34 | | | |
| Al ₂ O ₃ | n. d. | 0.05 | | | |
| H ₂ O ⁺ | 0.40 | n. d. | | | |
| H ₂ O ⁻ | 0.15 | n. d. | | | |
| | 100.02 | 100.45 | | 99.22 | 98.60 |
| Al ₂ O ₃ < 0.005 | | | | | |

Mg_{1.771}Fe_{0.214}Ni_{0.006}Ca_{0.009}(SiO₄) and Mg_{1.724}Fe_{0.260}Ni_{0.006}Ca_{0.009}(SiO₄). We first studied the Mg/Fe distribution over *M 1* and *M 2* in the natural untreated crystals. Then we subjected the crystals to various, well defined oxygen partial pressures and studied afterwards the crystals again by X-ray diffraction, thus determining the influence of the oxygen fugacity on the cation distribution.

2. Experimental procedures

a) Crystal selection

Small crystals ranging in size from 0.5 to 4.0 mm were separated from the nodules. From about two hundred crystals of *FE 10* and eighty crystals of *FE 12* only about 20 crystals were found to be free of twinning, intergrowth or cracks by examination under a polarization microscope. For the ensuing measurements on the four-circle-diffractometer these crystals were ground to spheres of about 0.2 mm diameter, a process which tends to introduce cracks. Finally 10 crystals *FE 10* and 5 crystals *FE 12* were available for X-ray investigations.

b) Data collection

The measurements were done on a computer controlled four-circle-diffractometer (Syntex *P 2*₁) with MoK α radiation ($\lambda = 0.71069 \text{ \AA}$) and a graphite monochromator ($2\theta = 12.2^\circ$). The unit cell parameters were determined by least squares calculations from the adjusted settings of 25 independent reflexions. The intensity data were collected in the $\theta - 2\theta$ scan mode with a 1.0° plus (α_1, α_2) dispersion scan range. The maximum value of 2θ was 80° ($\sin \theta/\lambda = 0.9 \text{ \AA}^{-1}$). The scan speed was adjustable between 0.5

Table 2. Summary of crystal data and data collection

| | | | | | | | |
|---------------------------------|--|---------------------------|----------------------------|-------------------------|----------------------------|----------------------------|----------------------------|
| Wave length: | $\lambda = 0.71069 \text{ \AA}$; $2\theta_{\max} = 80^\circ$ ($\sin \theta/\lambda = 0.9 \text{ \AA}^{-1}$) | | | | | | |
| Space group: | <i>Pnma</i> | | | | | | |
| Crystal size diameter: | 0.19–0.21 mm | | | | | | |
| | <i>FE 10</i> natural | <i>FE 10</i> <i>PU</i> | <i>FE 10</i> <i>P 1</i> | <i>FE 12</i> natural | <i>FE 12</i> <i>P 2</i> | <i>FE 12</i> <i>P 3</i> | <i>FE 12</i> <i>P 4</i> |
| $\mu(\text{MoK}\alpha)$ | 20 cm^{-1} | | | 22 cm^{-1} | | | |
| Number of refl. incl. stand. | 2483 | 2610 | 1578 | 2256 | 1976 | 2259 | 2499 |
| Unique refl. | 976 | 978 | 979 | 980 | 975 | 975 | 975 |
| Unobs. ($I < 2.5 \sigma$) | 164 | 110 | 138 | 120 | 59 | 59 | 36 |

Table 3. Lattice constants of the olivine crystals before (a) and after buffering (b), estimated standard deviations in parenthesis

| | | a_0 | b_0 | c_0 |
|------------------|-----|-----------|-----------|-------------|
| <i>FE 10</i> | (a) | 6.0027(9) | 4.7673(7) | 10.2391(10) |
| <i>FE 10 PU</i> | (b) | 6.0028(8) | 4.7673(6) | 10.2424(8) |
| <i>FE 10 P 1</i> | (b) | 6.0030(6) | 4.7679(5) | 10.2448(6) |
| <i>FE 12</i> | (a) | 6.005(1) | 4.7687(8) | 10.2773(11) |
| <i>FE 12 P 2</i> | (b) | 6.004(1) | 4.7678(6) | 10.2729(10) |
| <i>FE 12 P 3</i> | (b) | 6.004(1) | 4.7674(4) | 10.2719(10) |
| <i>FE 12 P 4</i> | (b) | 6.004(1) | 4.7676(8) | 10.2731(15) |

and 14.65° per minute and the total background counting time equalled the time spent for the peak count. Four standard reflexions 211 , $\overline{211}$, 113 , $\overline{113}$ were measured after every 30 reflexions. In the data reduction the intensities were adjusted to the fluctuations of the sums of the standards. Measurements were performed in the hkl and $hk\bar{l}$ octants, related reflexions were averaged resulting in a set of 980 unique reflexions for each crystal. Reflexions with $I < 2.5 \sigma$ were considered unobserved. No absorption correction was applied ($A = 1.80$ for $2\theta = 0^\circ$ and $A = 1.76$ for $2\theta = 80^\circ$ in the case of *FE 10*). The results of the crystal measurements and data collection are summarized in Table 2. Table 3 lists the lattice parameters of all crystals investigated, including the values of the crystals after buffer treatment.

c) Structure refinement

Refinements of the structures were carried out using a local version of the full matrix least squares program ORFLS (Busing, Martin, and Levy, 1962)

extended for the refinement of the occupation numbers on *M1* and *M2*. Atomic scattering factors were taken for Fe^{2+} , Mg^{2+} , Si^0 , O^0 from Cromer and Mann (1968). Anomalous scattering was considered for Fe (Cromer, 1965). The reflexions were weighted with their own sigmas [$w = 1/\sigma^2(F)$] as well as with a Cruickshank (1961) weighting scheme. All atoms were refined for anisotropic thermal vibration, secondary extinction were taken into account according to Zachariasen (1963).

The multiplicity factors in the least squares calculations scale the scattering factors and hence may serve to count the numbers of electrons assigned to each site effectively. From the multiplicity factors the occupation numbers can be calculated and from them the cation ordering.

A least squares refinement of site occupancies has to take into account constraints imposed by the chemical composition and the electroneutrality of the crystals. If we define a_{mn} as the fractional occupancy of the site *m* by the chemical species *n*, then the equation

$$\sum_n a_{mn} \leq 1 \quad (3)$$

must be satisfied as a first constraint. As a second constraint the site chemistry must agree with the bulk chemistry, known from the chemical analysis (Table 1). With c_n = the total number of atoms of the species *n* (Mg and Fe) per unit cell or per formula unit, and b_m the multiplicity of the site *m* we get

$$\sum_m b_m \cdot a_{mn} = c_n \quad (4)$$

The formal solution of this problem has been derived by Raymond (1972). For the present case we can express these conditions by a matrix:

| <i>n</i> \ <i>m</i> | <i>M1</i> | <i>M2</i> |
|---------------------|-----------|-----------|
| Fe | a_{11} | a_{12} |
| Mg | a_{21} | a_{22} |

c_1 and c_2 of Eq. (4) can be calculated from the chemical analysis. In the case of *FE10* we get $c_1 = 0.216$ (concentration of Fe-ions per formula unit), and $c_2 = 1.784$ (concentration of Mg-ions per formula unit). In the least squares calculation it suffices to refine only one variable, $V_1 = a_{11}$ (= Fe on *M1*), while the other parameters are determined through the constraints C_1 , C_2 and C_3 . This is compactly expressed in matrix notation.

$$Q = \begin{bmatrix} 1 & 0 & 0 & 0 \\ b_1 & b_2 & 0 & 0 \\ b_1 & 0 & b_3 & 0 \\ b_1 & b_2 \text{ Mg/Fe} & 0 & b_4 \text{ Mg/Fe} \end{bmatrix} \cdot \begin{bmatrix} a_{11} (\text{FeM1}) \\ a_{12} (\text{MgM1}) \\ a_{21} (\text{FeM2}) \\ a_{22} (\text{MgM2}) \end{bmatrix} = \begin{bmatrix} V_1 \\ C_1 \\ C_2 \\ C_3 \end{bmatrix} \quad (5)$$

The first constraint C_1 imposes the full occupancy of $M1$. The second constraint C_2 introduces the chemistry through the total amount of Fe known from the chemical analysis, and the third constraint C_3 contains the total charge at the positions $M1$ and $M2$, which is calculated from the chemical composition. From the values a_{mn} which have been determined by least squares refinement procedure for all crystals, the distribution coefficient K_D can be calculated (Eq. 1).

3. Crystal structure refinements

In total we have made seven measurements and structure refinements on the two types of crystals $FE10$ and $FE12$. Two measurements were on the original natural crystals and five measurements on the crystals after being treated by different buffering processes. The buffering conditions are summarized in Table 4.

a) Buffer treatment

Since we expect that the Mg/Fe distribution should depend on the oxygen partial pressure, we have treated the crystals by two pO_2 -pressures as defined by the two different buffer mixtures, namely QFM , consisting of quartz,

Table 4. Experimental data for the buffer treatments

| Sample | pO_2 (bar) | T (°C) | h | Buffer | |
|-----------------------------|-----------------|-------------|-----|---------------------------|-------|
| $FE10 \rightarrow FE10PU$ | 10^{-16} | 750 | 25 | $Fe_3O_4/SiO_2/Fe_2SiO_4$ | QFM |
| $(FE10) \rightarrow FE10P1$ | 10^{-21} | 750 | 20 | $Fe/SiO_2/Fe_2SiO_4$ | QFI |
| $FE12 \rightarrow FE12P2$ | 10^{-21} | 750 | 66 | $Fe/SiO_2/Fe_2SiO_4$ | QFI |
| $(FE12) \rightarrow FE12P3$ | 10^{-21} | 750 | 66 | $Fe/SiO_2/Fe_2SiO_4$ | QFI |
| ↓ | | | | | |
| $FE12P4$ | 10^{-16} | 750 | 24 | $Fe_3O_4/SiO_2/Fe_2SiO_4$ | QFM |

Table 5. Summary of R -values for all crystals studied

| | $FE10$ | $FE10P1$ | $FE10PU$ | $FE12$ | $FE12P2/3$ | $FE12P4$ |
|-------------------------|--------|----------|----------|--------|------------|----------|
| $R_{overall}$ | 0.0304 | 0.0361 | 0.0389 | 0.0263 | 0.0328 | 0.0228 |
| $R_{omitting\ unobs.}$ | 0.0208 | 0.0279 | 0.0337 | 0.0202 | 0.0300 | 0.0217 |
| $R_{weighted\ overall}$ | 0.0306 | 0.0363 | 0.0392 | 0.0255 | 0.0321 | 0.0220 |
| $R_{weight.om.unobs.}$ | 0.0198 | 0.0252 | 0.0331 | 0.0198 | 0.0274 | 0.0209 |

Table 6. Occupation numbers for Fe and Mg on the two sites (*M1*) and (*M2*), and distribution coefficient K_D

| | <i>(M1)</i> | | <i>(M2)</i> | | K_D |
|------------------|-------------|--------|-------------|--------|---------|
| | Fe | Mg | Fe | Mg | |
| <i>FE10</i> | 0.1124(7) | 0.8876 | 0.1036 | 0.8964 | 1.09(1) |
| <i>FE10 P1</i> | 0.1168(10) | 0.8832 | 0.0992 | 0.9008 | 1.20(2) |
| <i>FE10 PU</i> | 0.0974(10) | 0.9026 | 0.1186 | 0.8814 | 0.80(2) |
| <i>FE12</i> | 0.1394(5) | 0.8606 | 0.1336 | 0.8670 | 1.06(1) |
| <i>FE12 P2/3</i> | 0.1464(10) | 0.8526 | 0.1256 | 0.8744 | 1.20(2) |
| <i>FE12 P4</i> | 0.1380(8) | 0.8620 | 0.1340 | 0.8660 | 1.03(1) |

fayalite and magnetite, and *QFI*, consisting of quartz, fayalite and iron (Will and Nover, 1979). At constant $T = 750^\circ\text{C}$ we have a $p\text{O}_2$ pressure of 10^{-21} bar for *QFI* and of 10^{-16} bar for *QFM*. These values are determined by the buffer composition and the given temperature. After each buffer treatment the crystals were studied again as described by a complete X-ray diffraction analysis and their structures refined. The lattice constants of all crystals are included in Table 3, the corresponding *R*-values are given in Table 5 and the occupation numbers together with the occupation coefficients K_D in Table 6. The standard deviation of *FeM1* is given in parenthesis. The error of this value is about 0.4% for all crystals ($K_D = \pm 1.5\%$). Figure 1 depicts the K_D distribution coefficient of this paper together with previous measurements taken from literature.

b) Atomic positions and bond length

The atomic positions and temperature factors are listed in Tables 7 and 8 for all crystals of composition *FE10* and *FE12*. Figure 2 depicts an ORTEP-drawing of the structural section containing *M1* and *M2* showing the coordination of these sites. From the atomic positions interatomic distances were calculated and selected values are given in Table 9. The mean *M1*–O, *M2*–O and Si–O distances are plotted in Figure 3 together with values reported in the literature. Within the same composition no differences in the bond length of the mean *M1*–O and *M2*–O distances are to be observed implying that there is no correlation between K_D and the bond length. The same observation holds for the bond angles, which are tabulated in Table 10.

c) Temperature factors

Anisotropic temperature factors were included in the refinement, and the results are included in Tables 8 and 9. We realize that the temperature factors

Table 7. Atomic coordinates for the seven olivines

| | | <i>FE 10</i> | <i>FE 10 P 1</i> | <i>FE 10 PU</i> | <i>FE 12</i> | <i>FE 12 P 2/3</i> | <i>FE 12 P 4</i> |
|-------------|----------|--------------|------------------|-----------------|--------------|--------------------|------------------|
| <i>(M1)</i> | <i>x</i> | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | <i>y</i> | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | <i>z</i> | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| <i>(M2)</i> | <i>x</i> | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 |
| | <i>y</i> | -0.0103(1) | -0.0107(2) | -0.0102(2) | -0.0104(2) | -0.0105(2) | -0.0105(2) |
| | <i>z</i> | 0.27773(6) | 0.27773(9) | 0.27776(9) | 0.27782(8) | 0.27782(8) | 0.27779(6) |
| Si | <i>x</i> | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 |
| | <i>y</i> | 0.4267(1) | 0.4268(1) | 0.4268(1) | 0.4270(1) | 0.4268(1) | 0.42688(9) |
| | <i>z</i> | 0.09446(5) | 0.09445(6) | 0.09436(6) | 0.09454(5) | 0.09455(5) | 0.09458(2) |
| O1 | <i>x</i> | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 |
| | <i>y</i> | 0.7662(2) | 0.7659(3) | 0.7661(3) | 0.7660(3) | 0.7659(3) | 0.7662(2) |
| | <i>z</i> | 0.0917(1) | 0.0916(1) | 0.0920(2) | 0.0918(1) | 0.0917(1) | 0.0916(1) |
| O2 | <i>x</i> | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 |
| | <i>y</i> | 0.2208(2) | 0.2206(3) | 0.2203(3) | 0.2203(3) | 0.2205(3) | 0.2199(2) |
| | <i>z</i> | 0.4475(1) | 0.4476(1) | 0.4476(1) | 0.4477(1) | 0.4478(1) | 0.4478(1) |
| O3 | <i>x</i> | 0.0336(1) | 0.0333(2) | 0.0333(2) | 0.0334(1) | 0.0332(2) | 0.0335(1) |
| | <i>y</i> | 0.2784(2) | 0.2785(2) | 0.2786(2) | 0.2788(2) | 0.2786(2) | 0.2787(1) |
| | <i>z</i> | 0.1634(1) | 0.1634(1) | 0.1634(1) | 0.1634(1) | 0.1633(1) | 0.16333(7) |

Table 8. Anisotropic temperature factors for the olivines ($\times 10^{-4}$)

| | | <i>FE 10</i> | <i>FE 10 P 1</i> | <i>FE 10 P U</i> | <i>FE 12</i> | <i>FE 12 P 2/3</i> | <i>FE 12 P 4</i> |
|--------------|---------------|--------------|------------------|------------------|--------------|--------------------|------------------|
| <i>(M 1)</i> | β (1,1) | 29(2) | 31(2) | 27(2) | 26(1) | 37(3) | 25(1) |
| | (2,2) | 37(2) | 57(3) | 43(3) | 36(2) | 54(3) | 39(2) |
| | (3,3) | 13.7(5) | 11.0(6) | 12.3(7) | 12.3(5) | 12.0(6) | 12.6(4) |
| | (1,2) | 3(1) | 3(2) | 4(2) | 4(1) | 3(2) | 4(1) |
| | (1,3) | 3.8(7) | 3.7(9) | 3.2(8) | 4(1) | 4(1) | 4(1) |
| | (2,3) | 1.3(1) | 1.2(1) | 1.3(1) | 0.7(1) | 1.0(1) | 0.4(9) |
| <i>(M 2)</i> | β (1,1) | 33(2) | 34(2) | 38(2) | 31(1) | 37(3) | 31(1) |
| | (2,2) | 51(2) | 69(3) | 66(3) | 54(3) | 67(3) | 57(2) |
| | (3,3) | 9(4) | 7(6) | 7(7) | 9.5(5) | 7.9(5) | 9.0(2) |
| | (1,2)=(1,3) | 0 | 0 | 0 | 0 | 0 | 0 |
| | (2,3) | 0.40(9) | 0.1(1) | 0.1(1) | 0.70(9) | 1.0(1) | 1.0(1) |
| Si | β (1,1) | 27.5(9) | 31(1) | 28(1) | 23.9(9) | 33(2) | 23.3(8) |
| | (2,2) | 26(1) | 41(2) | 37(2) | 27(1) | 43(2) | 29(1) |
| | (3,3) | 9(3) | 7(4) | 7(4) | 7.9(3) | 7.2(3) | 8.4(2) |
| | (1,2)=(1,3) | 0 | 0 | 0 | 0 | 0 | 0 |
| | (2,3) | 0.2(9) | 1(7) | 0.4(7) | 0.2(6) | 0.7(6) | 1.3(4) |
| O1 | β (1,1) | 41(3) | 41(3) | 22(3) | 34(2) | 43(5) | 32(2) |
| | (2,2) | 46(4) | 48(5) | 42(5) | 33(4) | 47(4) | 36(3) |
| | (3,3) | 10(1) | 13(1) | 20(1) | 15.3(8) | 13.8(9) | 14.3(9) |
| | (1,2)=(1,3) | 0 | 0 | 0 | 0 | 0 | 0 |
| | (2,3) | 2(1) | 2(2) | 2(2) | 0.1(1) | 0.1(1) | 0.1(1) |
| O2 | β (1,1) | 42(3) | 42(3) | 21(3) | 38(2) | 46(5) | 36(2) |
| | (2,2) | 46(4) | 66(5) | 60(5) | 50(4) | 60(5) | 55(3) |
| | (3,3) | 10(1) | 7.5(9) | 16(1) | 9.3(8) | 8.3(9) | 9.6(6) |
| | (1,2)=(1,3) | 0 | 0 | 0 | 0 | 0 | 0 |
| | (2,3) | 2(1) | 1(2) | 1(2) | 1(1) | 1(1) | 1(1) |
| O3 | β (1,1) | 37(2) | 37(2) | 19(2) | 37(2) | 40(4) | 33(1) |
| | (2,2) | 46(3) | 69(3) | 59(3) | 49(3) | 64(3) | 51(2) |
| | (3,3) | 14(5) | 13(5) | 19(6) | 13.9(5) | 12.7(6) | 13.5(4) |
| | (1,2) | - 3(2) | - 1(2) | - 3(2) | - 2(2) | - 2(2) | - 2(1) |
| | (1,3) | 5.1(8) | 5(1) | 5(1) | 4.4(8) | 3.0(1) | 4.8(7) |
| | (2,3) | 0.6(9) | 7(1) | 3(1) | 0.2(1) | 0.1(1) | 0.2(1) |

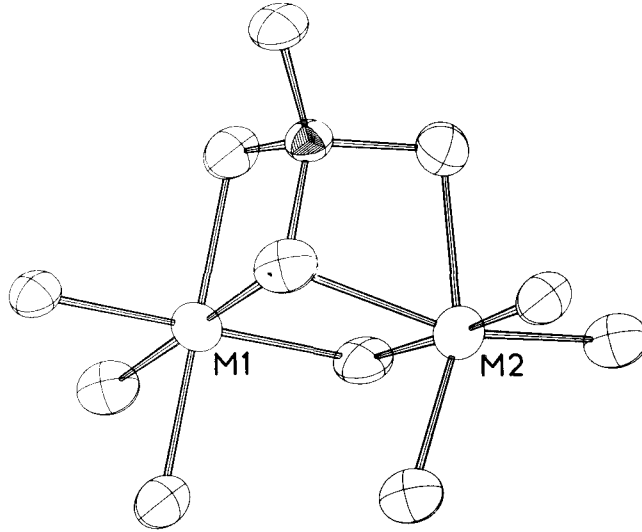


Fig. 2. An ORTEP drawing of a section of the structure of olivine around *M1* and *M2* showing the tetrahedral and octahedral coordination of Si and of the cations resp.

for the buffered crystals are larger than those for the original natural crystals *FE10* and *FE12*. Since a change in K_D means an exchange of Mg and Fe between the sites *M1* and *M2* this process may well introduce structural defects and therefore higher vibrational coefficients. Figure 2 allows one to see this anisotropy of the polyeder *M1*, *M2* and Si with the surrounding oxygen atoms.

d) Extinction

Some strong low angle reflexions showed large discrepancies in the first stages of the refinement. A correction for isotropic secondary extinction was therefore included in the refinement according to Zachariasen (1968). The results are included in Tables 7 and 8. The buffered crystals have larger *g*-values than the natural untreated crystals, indicating that the process of buffering introduces structural defects, which is not surprising.

e) Charge density

Wenk and Raymond (1973) have calculated approximated formal electrical charges for each atom from the refined scale factors. Such results cannot be conclusive and accordingly their calculations did not converge. The proper

Table 9. Selected interatomic distances

| | <i>FE 10</i> | <i>FE 10 P 1</i> | <i>FE 10 PU</i> | <i>FE 12</i> | <i>FE 12 P 2/3</i> | <i>FE 12 P 4</i> |
|-----------------------|--------------|------------------|-----------------|--------------|--------------------|------------------|
| (1) Si–O(1) | 1.619(1) | 1.618(2) | 1.618(2) | 1.616(2) | 1.616(2) | 1.618(1) |
| (1) Si–O(2) | 1.661(1) | 1.661(2) | 1.658(2) | 1.660(2) | 1.659(2) | 1.662(1) |
| (2) Si–O(3) | 1.639(1) | 1.640(1) | 1.641(1) | 1.640(2) | 1.639(1) | 1.639(1) |
| ⟨Si–O⟩ | 1.639(1) | 1.639(2) | 1.639(2) | 1.639(2) | 1.638(2) | 1.639(1) |
| (2) <i>M 1</i> –O(1) | 2.092(1) | 2.093(1) | 2.094(1) | 2.094(2) | 2.092(1) | 2.093(1) |
| (2) <i>M 1</i> –O(2) | 2.077(1) | 2.078(1) | 2.078(1) | 2.079(2) | 2.076(1) | 2.079(1) |
| (2) <i>M 1</i> –O(3) | 2.145(1) | 2.147(1) | 2.146(1) | 2.147(1) | 2.145(1) | 2.150(1) |
| ⟨ <i>M 1</i> –O⟩ | 2.105(1) | 2.106(1) | 2.106(1) | 2.107(2) | 2.104(1) | 2.107(1) |
| (1) <i>M 2</i> –O(1) | 2.183(2) | 2.185(2) | 2.181(2) | 2.184(2) | 2.184(2) | 2.189(1) |
| (1) <i>M 2</i> –O(2) | 2.058(2) | 2.060(2) | 2.058(2) | 2.059(2) | 2.060(2) | 2.064(1) |
| (2) <i>M 2</i> –O(3) | 2.068(1) | 2.066(1) | 2.066(1) | 2.066(2) | 2.066(1) | 2.067(1) |
| (2) <i>M 2</i> –O(3') | 2.226(1) | 2.229(2) | 2.226(1) | 2.229(2) | 2.228(1) | 2.230(1) |
| ⟨ <i>M 2</i> –O⟩ | 2.138(2) | 2.139(2) | 2.137(2) | 2.139(2) | 2.138(1) | 2.141(1) |

Table 10. Selected bond angles

| | <i>FE 10</i> | <i>FE 10 PU</i> | <i>FE 10 P 1</i> | <i>FE 12</i> | <i>FE 13 P 2/3</i> | <i>FE 12 P 4</i> |
|--------------------|--------------|-----------------|------------------|--------------|--------------------|------------------|
| 1 O(1)–Si–O(2) | 114.03(9) | 114.09(9) | 114.01(9) | 114.05(8) | 113.98(9) | 113.85(6) |
| 2 O(1)–Si–O(3) | 116.05(5) | 115.93(6) | 116.03(6) | 116.00(5) | 116.00(5) | 116.03(4) |
| 2 O(2)–Si–O(3') | 101.97(6) | 102.03(7) | 101.98(6) | 101.98(5) | 101.96(6) | 102.07(4) |
| 1 O(3)–Si–O(3') | 104.87(7) | 104.97(8) | 104.93(7) | 104.96(6) | 105.06(7) | 104.92(5) |
| ⟨O–Si–O⟩ | 109.16(5) | 109.16(7) | 109.19(7) | 109.16(8) | 109.16(6) | 109.16(4) |
| 2 O(1)–M 1–O(3) | 84.97(5) | 84.99(6) | 85.05(6) | 84.98(5) | 85.01(5) | 84.90(4) |
| 2 O(1)–M 1–O(3') | 95.03(5) | 95.01(6) | 94.95(6) | 95.02(5) | 94.99(5) | 95.10(4) |
| 2 O(1)–M 1–O(2') | 93.48(5) | 93.43(5) | 93.43(5) | 93.44(4) | 93.51(4) | 93.44(3) |
| 2 O(1')–M 1–O(2') | 86.52(5) | 86.57(5) | 86.57(5) | 86.56(4) | 86.49(4) | 86.56(3) |
| 2 O(2)–M 1–O(3') | 105.23(5) | 105.24(5) | 105.24(5) | 105.30(5) | 105.27(5) | 105.28(4) |
| 2 O(2)–M 1–O(3) | 74.77(5) | 74.76(6) | 74.76(5) | 74.70(5) | 74.73(5) | 74.72(4) |
| ⟨O–M 1–O⟩ | 90.00(5) | 90.00(6) | 90.00(6) | 90.00(5) | 90.00(5) | 90.00(4) |
| 2 O(1)–M 2–O(3'') | 90.95(5) | 90.90(5) | 90.99(5) | 90.96(5) | 91.02(5) | 91.10(3) |
| 2 O(1)–M 2–O(3') | 80.95(5) | 81.06(6) | 80.97(5) | 80.97(5) | 80.90(5) | 80.80(4) |
| 2 O(2)–M 2–O(3'') | 90.84(5) | 90.80(5) | 90.80(5) | 90.78(5) | 90.75(5) | 90.64(3) |
| 2 O(2)–M 2–O(3') | 96.50(6) | 96.55(5) | 96.48(6) | 96.56(5) | 96.58(6) | 96.73(4) |
| 1 O(3')–M 2–O(3'') | 71.43(5) | 71.55(5) | 71.41(5) | 71.39(5) | 71.45(5) | 71.30(4) |
| 2 O(3')–M 2–O(3) | 88.50(4) | 88.48(5) | 88.53(4) | 88.49(4) | 88.49(5) | 88.56(3) |
| 1 O(3')–M 2–O(3) | 110.84(6) | 110.76(6) | 110.82(6) | 110.91(6) | 110.86(6) | 110.87(4) |
| ⟨O–M 2–O⟩ | 89.89(4) | 89.84(5) | 89.81(5) | 89.82(6) | 89.82(5) | 89.82(4) |

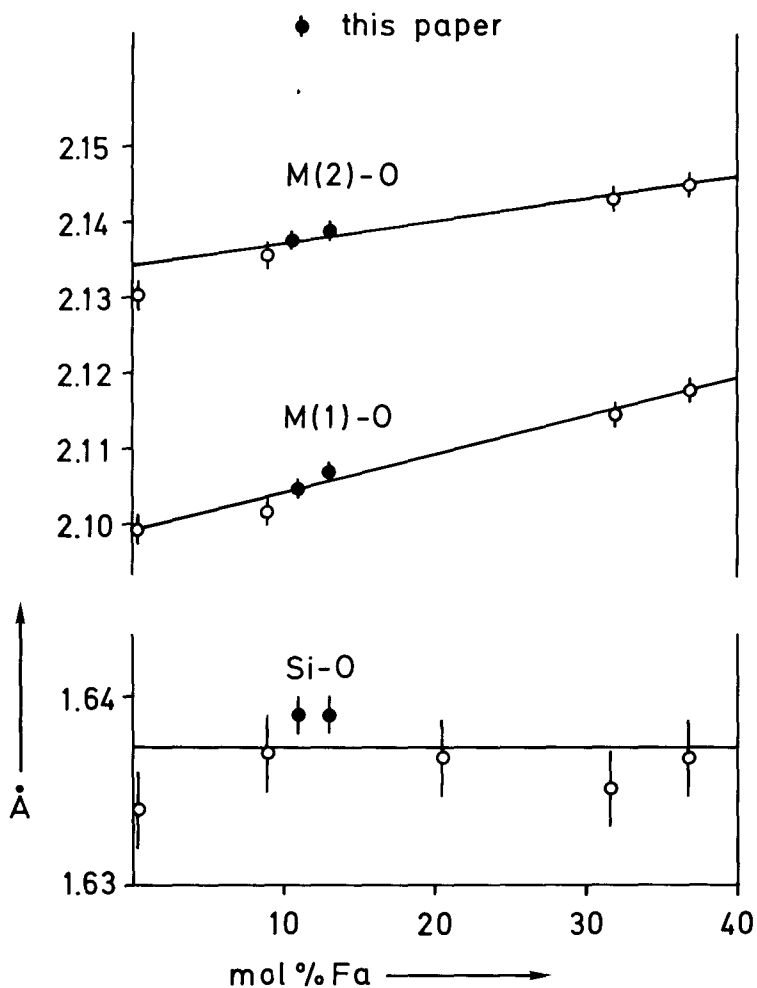


Fig. 3. The mean $M1-O$, $M2-O$ and $Si-O$ distances as a function of the fayalite content for several olivines, including selected results from the literature

way to calculate the formal charge of the SiO_4 tetrahedra is by interpretation of the electron densities from difference Fourier maps as shown in Figure 4. We have studied recently bonding features and point charges in the $[S_2O_6]^{2-}$ complex of $Na_2S_2O_6 \cdot 2H_2O$ (Kirfel, Will, and Weiss, 1979) and in the $[SO_4]^{2-}$ tetrahedron of $CaSO_4$ (Kirfel and Will, 1980) and we have applied this method also to the $[SiO_4]^{4-}$ tetrahedron. Different structural models based on the refined multiplicity factors for Si and oxygen were selected and

