

Determination of site population in olivine: Warnings on X-ray data treatment and refinement

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ABSTRACT

Leverage analysis enables identification of reflections with the greatest influence on the estimate of each refined variable, and thus may be an important tool to improve standard structure-refinement procedures, especially in the case of minerals with complex composition. In this work, leverage analysis was used to investigate in detail the influence of each reflection in high-resolution X-ray diffraction data collected from olivine, a mineral often used to model order-disorder processes and to calculate temperatures of closure and cooling rates of host rocks. Particular attention was paid to the estimate of the scattering power at the cation sites, that are crucial for the above studies. Various procedures for data correction and refinement were also investigated, and the different possible choices were compared to choose the strategy that provides the best results.

The presence of high-leverage weak reflections in olivine strongly suggests that systematic data truncation according to intensity threshold should be avoided. The estimates of the site-scatterings obtained under the different conditions tested are very close (always $\leq 3\sigma$); they are often smaller than those which may be obtained from electron-microprobe analysis under different experimental conditions or on inhomogeneous (zoned) crystals. Chemical data should thus not be routinely used to constrain the refinement procedure and/or to optimize final site-populations, provided that appropriate errors are given; on the other hand, they are valuable to appreciate the presence and the amounts of very minor, sometimes unexpected, substituents. Our tests show that precision better than 0.001 in site-occupancy determination (sometimes claimed in the literature) is probably not achieved.

PREVIOUS WORK AND INTRODUCTION

Leverage analysis, introduced by Prince and Nicholson (1985) to allow identification of the data points that most strongly affect the estimate of a refined variable in a least-squares procedure, is a powerful tool to improve the strategy for the structure refinement of minerals and to validate the reliability of its results. We recently applied leverage analysis to high-resolution X-ray diffraction data collected from two samples which represent extreme situations within rock-forming minerals: (1) a garnet, cubic, space group $Ia\bar{3}d$, with four structural sites, only one of which is in a general position, (2) an amphibole, monoclinic, space group $C2/m$, with 14 to 18 structural sites most of which in general position (Merli et al. 2000). We found that high-resolution data ($\sin\theta/\lambda \geq 0.8 \text{ \AA}^{-1}$) are crucial to obtain reliable structure-refinement results for simple and highly symmetric structures such as garnet, and that truncation of low- θ reflections is dangerous when estimating the scattering power at the structural sites (hereafter called site scattering) for both samples.

Here we examine the problems that may be encountered during the structure refinement of olivine, another widespread group of rock-forming minerals that is intermediate between garnets and amphiboles both for symmetry and complexity.

Olivine is frequently used in thermodynamic and kinetic calculations, as the degree of order of the Fe^{2+} -Mg distribution between the two independent octahedral sites (M1 and M2) can be related to the temperature of closure of the exchange process and to the cooling rate of the host rock.

The determination of the site populations at the M1 and M2 sites in olivine is usually based on: (1) their refined site-scatterings; (2) their geometrical features (mainly mean bond-lengths, mbl); (3) constraints from the electron-microprobe analysis; (4) crystal-chemical assumptions for the site preference of the minor constituents (Ca and trivalent cations). The estimate of the site scattering is the basis of the procedure, and its accuracy and precision are thus crucial.

A precision of ± 0.0007 in the (Mg vs. Fe^{2+}) occupancies at the M1 and M2 sites in orthopyroxene (the highest precision claimed so far) may give calculated cooling rates ranging from 0.06 to 0.6 °C/y (Kroll et al. 1997). Moreover, different (albeit highly precise) strategies applied in two top-level laboratories on two distinct orthopyroxene crystals separated from the same portion of a meteorite resulted in equilibration temperatures of 388 and 467 °C, and in cooling rates of 0.2 and 18 °C/y, respectively (Zema et al. 1996; Kroll et al. 1997), which should be considered satisfactory agreement given all the sources of random and systematic errors (Kroll et al. 1997). The need for reliable estimate of the site populations is even more critical in olivine than in orthopyroxene because: (1) Fe^{2+} /Mg ordering is

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a complex function of temperature (and composition), as Fe^{2+} is preferentially incorporated into the larger M2 site at temperature (T) < 880 °C but into the smaller M1 site at higher T (Aikawa et al. 1985; Ottonello et al. 1990; Artioli et al. 1995; Henderson et al. 1996; Rinaldi et al. 1997; Heinemann et al. 1999); (2) f_{O_2} affects the ordering process (Ottonello et al. 1990; Chakraborty 1997); (3) the inverse dependence of the cation partitioning coefficient, i.e., $[K_D = (\text{Fe}_{\text{M1}} \cdot \text{Mg}_{\text{M2}}) / (\text{Fe}_{\text{M2}} \cdot \text{Mg}_{\text{M1}})]$ on T has a much smaller slope than in orthopyroxene, a wider range of T being thus compatible with variations of the site populations within e.s.d.

We used residual analysis and leverage analysis to investigate the consequences on the refinement results (especially on site scattering) of different procedures of data reduction and least-squares refinement in the case of olivine. Both approaches were used in all the steps; however, the final leverage analysis was done on the “best” model obtained after settling on procedures for data treatment and refinement. The tests were done on solely one crystal with composition similar to those used in kinetic studies, but have general validity for olivine especially in the relevant forsterite (Fo)-fayalite (Fa) join. In fact, the strictly coherent behavior found within the two complex mineral families so far investigated (garnet and amphibole; Merli et al. 2000) can be extended to the much simpler solid-solution pattern observed in olivine (i.e., mainly the $\text{Fe}^{2+}\text{Mg}_{-1}$ exchange).

This work is aimed solely to improve the data treatment and least-squares refinement procedures that are commonly used for geothermobarometric and geospeedometric purposes. More sophisticated procedures for data treatments (e.g., analytical absorption correction and theoretical corrections for secondary extinction and Renninger effect) and refinement (e.g., multipole refinement) should be used to obtain a better approximation to the real values and a more physically consistent model of the electron density and of the derived properties. However, these more complex and time-consuming methods are appropriate for detailed electron-density studies, but are impractical when a large number of refinements (on several crystals annealed at several temperatures for several different and increasing times) must be done to obtain estimates of the closure temperature and of the cooling rate for any mineral composition. Therefore, we decided to work on an olivine crystal with standard optical and diffracting behavior, for which unit-cell parameters were measured and diffracted intensities were collected and treated in a way similar to (sometimes even more accurate than) those reported in the relevant literature.

DATA COLLECTION AND CHEMICAL ANALYSIS

The selected single crystal of olivine from an unknown locality (with averaged radius = 0.25 mm) has composition $\text{Fo}_{92}\text{Fa}_{08}$, space group $Pbnm$, $a = 4.7579$ (1) Å, $b = 10.2151$ (2) Å, $c = 5.9890$ (2) Å, $V = 291.18$ Å³. X-ray analysis was done at room temperature on a Philips PW-1100 diffractometer with graphite-monochromatised $\text{MoK}\alpha$ radiation. Unit-cell dimensions were calculated from least-squares refinement of the d values obtained from 60 rows of the reciprocal lattice by measuring the centroid of each reflection in the range $-30 < \theta < +30$ °. Data were collected up to $\theta = 67.5$ °. We measured 5991 reflections in the region of the reciprocal space with $\pm h, +k, +l$,

using a scan width of 2.5 °, a $\omega/2\theta$ scan mode, and a scan speed of 0.08°/s. Three standard reflections (400, 0100 and 060) were measured every 300 reflections to monitor the stability of the primary X-ray beam; their long-time variations were within 2.0%. A spherical absorption coefficient (μ) of 39.9 cm⁻¹ was used, and the data were also semi-empirically corrected for absorption according to North et al. (1968). Intensities were then corrected for Lorentz-polarization, and merged by applying a weight equal to $1/\sigma$ to each equivalent reflection. R_{sym} was 1.9% for the 2732 unique reflections.

Electron-microprobe analysis was done with a JEOL JXA-840A microprobe using mineral standards; 10 point analyses were averaged, and the unit formula was calculated on the basis of 4 oxygen atoms, giving $\text{Mg} = 1.849(4)$, $\text{Fe} = 0.151(2)$, $\text{Si} = 0.999(3)$, $\text{Al} = 0.001(1)$.

DATA REDUCTION

Figure 1 shows the intensities of the measured reflections plotted against the signal-to-noise ratio before applying any data reduction procedure. We propose this test to detect anomalies due to instrumental problems such as X-ray beam fluctuation or to crystal imperfections such as inclusions, unbalanced backgrounds, and large thermal diffuse scattering, which would appear as discontinuities or shifted trends. These features are not present in the nearly ideal parabolic trend shown by the set of diffracted intensities used in this work.

The empirical correction for absorption was done at first by combining distinct absorption curves measured for two distinct reflections at different $\sin\theta/\lambda$ values. We obtained 83 independent reflections with $\sqrt{[1/n \sum_{j=1,n} (F_{0j}^2 - F_0^2)^2 / (n-1)]} > \sigma_{F_0}$ (“inconsistent equivalent reflections” in SHELX terminology); they reduced to 72 when using only one absorption curve. Strictly analogous results had always been obtained at the CNR-CSCC when processing high-resolution data collected on mineral crystals, suggesting that interpolation of empirical absorption curves at different $\sin\theta/\lambda$ values is still an unreliable procedure.

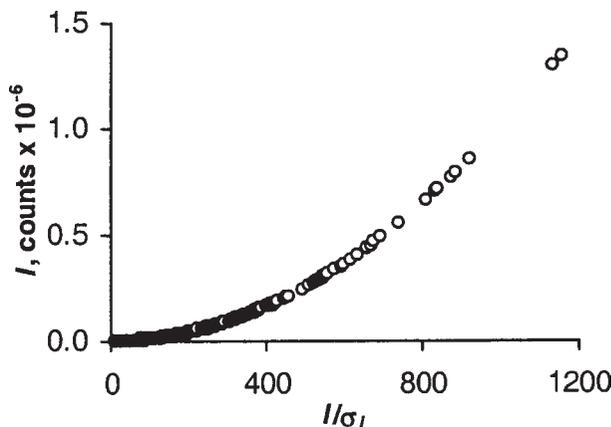


FIGURE 1. The intensities of the 5991 reflections collected up to $\theta = 67.5$ ° ($\text{MoK}\alpha$) plotted against their I/σ_I ratio. The nearly ideal parabolic trend discards the presence of errors due to instrumental problems or to crystal imperfections.

Another critical procedure is merging equivalent reflections. Its usefulness in improving the quality of the data has been reviewed by Blessing (1987), who proposed an algorithm that takes into account the variances of the single equivalent reflections. In general, two strategies can be followed during merging: (1) calculation of arithmetic or weighted means, with several options available for the weighting scheme; (2) attribution of an error equal to the variance of the equivalents to the reflections with variance higher than a given threshold. The latter is the most common practice in crystallography after its recommendation by IUCr (Schwarzenbach et al. 1989). When dealing with high-quality data such those from minerals, the "classical" weighted mean would have the double advantage of avoiding both the presence of two distinct populations of errors in the same data set and the use of (arbitrary) penalties for weak reflections.

The data set of this work was thus merged both arithmetically and by using $1/\sigma$ weights, and refined on $|F_o|$ with the program CRYSTALS (Watkin et al. 1996) using the recommended weighting scheme based on the optimization of the 3-parameters Chebyshev polynomials that fit the residuals (Carruthers and Watkin 1979; cf. below for further discussion); 192 and 10 reflections, respectively, were assigned zero weights in the refinement and considered as outliers. Thus a correct merging procedure is critical when many equivalents are collected due to symmetry or to experimental reasons (e.g., the use of area detectors).

An empirical correction for the Renninger effect was applied using a UNIX program available at the CNR-CSCC (F. Mazzi, personal communication). This program calculates the variations (gain or loss) in the intensity of each reflection (hkl , I_1) that are due to the other reflections ($h'k'l'$ and $h-h' k-k' l-l'$, with intensities I_2 and I_3 , respectively) within the limiting sphere that simultaneously satisfy the Bragg equation. The gain in I_1 is considered proportional to the product $I_2 \cdot I_3$, and the loss in I_1 is considered proportional to the product $I_1 \cdot I_3$. The sums of the positive and negative contributions due to the Renninger effect are then multiplied by two coefficients which are allowed to vary during the refinement procedure to give the best agree-

ment between F_o and F_c . Albeit empirical, this method has proven to be effective in the correction of overestimated intensities of weak reflections; underestimated intensities (of strong reflections) are actually adjusted (and thus masked) prevalently by the algorithms for the secondary extinction. Figures 2a and 2b show the corrections that were applied to the F_c (in absolute scale) because of the Renninger effect. A total of 539 weak reflections (out of the 5991 in our data set) distributed over the entire resolution range turned out to be significantly affected. Leverage analysis showed that some of these reflections strongly affect the estimate of variables relevant to the present discussion, in particular of the diagonal components of the atom displacement tensor at the M1 and M2 sites. In any case, correction for the Renninger effect improved the figures of merit of the refinement (R) and Goodness of Fit (GooF), and reduced violations of the systematic absences; it is thus recommended anytime highly precise results are required. Again, more correct and complete analytical corrections of the Renninger effect may be obtained [see for instance Chang (1984) and Rossmanith et al. (1990)], but are beyond the purposes of this work.

STRATEGIES FOR LEAST-SQUARES REFINEMENT

Stimpfl et al. (1999) compared site occupancies obtained by using the programs RFINE-90 (updated after Finger and Prince 1975) and SHELX-93 (Sheldrick 1993) for a series of experimentally heated orthopyroxene crystals with different compositions. The results were compatible within e.s.d. values, and the use of ionic scattering curves for Si (2.5+) and for O (1.5-) yielded better GooF and R_w indices as well as lower e.s.d. on site occupancies. Moreover, e.s.d. values from weighted refinements were systematically lower than those from unweighted refinement on selected reflections ($I/\sigma_I \geq 3-5$).

To extend these results, we refined the set of intensities collected on olivine by using other available least-squares programs: a locally rewritten version of ORFLS (modified after Busing et al. 1962), SHELX-93 and SHELX-97 (Sheldrick 1993, 1997, both in the PC and in the UNIX version), and CRYSTALS (Watkin et al. 1996), in which we selected the robust-resistant weighting scheme (see below for a discussion

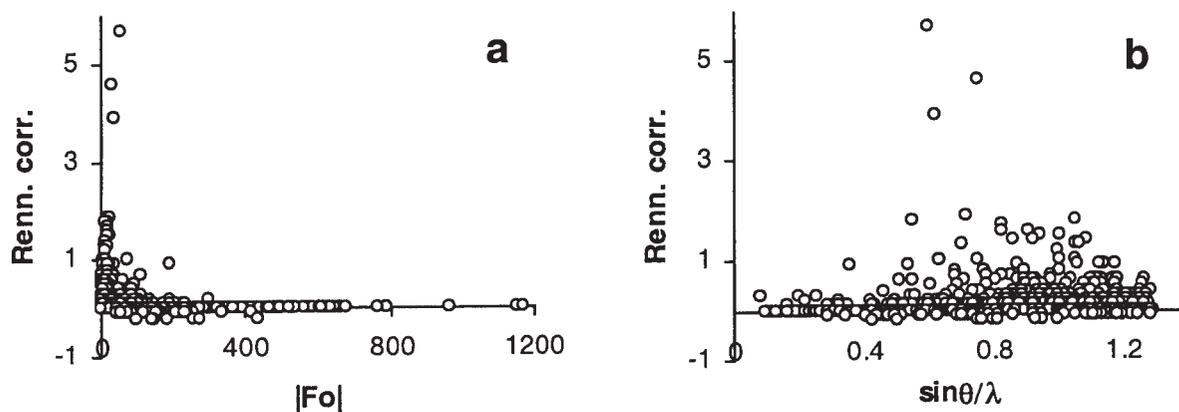


FIGURE 2. Analysis of the corrections for the Renninger effect applied to the F_c of the present data set.

on weighting schemes). In all the runs in the present work, we did full-matrix least-squares refinement, and used the symmetry requirements as constraints. The above programs use different approaches: ORFLS minimizes the function $\sum_j w_j (|F_{o,j}| - |F_{c,j}|)^2$, SHELX-93/97 the difference $\sum_j w_j (|F_{o,j}|^2 - |F_{c,j}|^2)^2$, and CRYSTALS allows both choices. When comparing solely the PC and the UNIX platforms for SHELX under the same conditions, we found discrepancies up to ± 0.001 for site occupancies that may derive from the different precision used by the computers.

The physically meaningful quantity refined is the scattering power at a given site, which can be expressed in terms of occupancy of one of the two selected scattering curves allowed to vary under the constraint that their sum is unity. The use of occupancies (e.g., ${}^{\text{M1}}X_{\text{Mg}}$) may be a reasonable approximation in olivines and in most orthopyroxenes, in which Mg and Fe are the only significant substituents, but is not a good approximation in more complex minerals. Henceforth, we refer to site scattering (in electrons per formula unit, epfu), bearing in mind that a precision of ± 0.001 in terms of X_{Mg} must be converted into ± 0.014 in terms of site scattering [$0.001 \times (Z_{\text{Fe}} - Z_{\text{Mg}})$].

To test the performances of the above programs, we calculated the theoretical structure factors from our "best" model [that with M1 and M2 site-scattering equal to 13.126(13) and 13.010(13) epfu; Table 1a], appended to them errors equal to those observed, and used them as input for the least-squares programs. The final refined geometrical parameters were practically identical in all the runs; however, best estimates of the site scattering were obtained by CRYSTALS either working on $|F_o|$ or F_o^2 (13.123 and 13.012 epfu or 13.124 and 13.012 epfu). Within the SHELX philosophy, SHELX-97 gave quite satisfactory results (13.092 and 12.980 epfu) whereas SHELX-93 gave 12.672 and 12.630 epfu, unacceptably low with respect to both the input values and the chemical analysis.

Choice of the model

Stimpfl et al. (1999) showed that the use of a (fixed) partially ionized model gives better statistics in the refinement results. Previous work at the CNR-CSCC (cf. Merli et al. 2000 and Hawthorne et al. 1995 for a list of references) showed that best results in terms of accuracy and physical meaningfulness of the model are obtained by: (1) using fully ionized scattering-factors of the major constituents in the sites where isomorphous substitutions occur, and deriving their relative occupancies so as to obtain the best estimate of the site scattering; (2) deriving neutral vs. fully ionized scattering-factors at the O (O vs. O^{2-}) and T (Si vs. Si^{4+}) sites where no chemical substitution occurs, so as to roughly estimate the ionization state. This procedure also increases the degrees of freedom of the system and, consequently, lowers the errors on the estimates of other variables.

In all the structural sites, the variables affected by symmetry restrictions (coordinates and harmonic atom-displacement parameters) were kept fixed (e.g., constrained); the sum of the occupancy factors (of the scattering polynomials) was constrained to unity, because the more critical procedure of restraining is not needed in the case of two atomic species. No chemical restraints were applied to avoid perturbation of the

least-squares procedure. In general, much care should be taken when applying restraints from chemical analysis, which might be affected by errors due to imperfect setting of the experimental conditions, to crystal inhomogeneity and also to incorrect site assignment. Moreover, albeit weighted for their standard deviations, restraints modify the least-squares algebra in such a way that the correlation can be strongly enhanced.

Secondary extinction coefficient

Different formulae for the estimate of the secondary extinction coefficient are used in the various programs tested. ORFLS uses that derived by Coppens and Hamilton (1970), CRYSTALS that by Larson (1969), whereas SHELX-93 and SHELX-97 refine an extinction parameter x to be used for correcting F_c by $k(1 + 0.001 \times F_c^2 \lambda^3 / \sin 2\theta)^{1/4}$, where k is the overall scale factor. Our tests showed that the octahedral site-scatterings are the most sensitive variables to the secondary extinction correction, which is thus crucial when accurate results are required. A few low- θ reflections have very high leverage values on the secondary extinction coefficient in olivine (see below). Therefore, the theoretical formulations derived by Larson (1969) and by Coppens and Hamilton (1970) should be preferred to the empirical correction used in SHELX, that has been optimized mostly for organic compounds. Indirect evidence in favor of the Larson (1969) correction comes from the analysis of electron-density maps obtained at the CNR-CSCC by the Maximum Entropy Methods (Collins 1982) from different crystals with the same composition or from different compositions within a given compositional join. They are far more consistent and comparable when structure-factors corrected according to Larson (1969) are used (Merli, unpublished work).

More sophisticated extinction modeling has been provided by Becker and Coppens (1974) and by Sabine (1988); however, they are not available in the packages we have tested, which are among those most commonly used in the relevant literature.

$|F_o|$ vs. F_o^2 , and the choice of the weighting schemes

The preference for $|F_o|$ or F_o^2 refinement is still under debate among crystallographers (Schwarzenbach et al. 1989). In the presence of sub- or super-structures (i.e., when the weakest reflections contain fundamental information), the best choice should be $|F_o|$ refinement as the leverage of the weakest data points is significantly reduced by squaring (Prince and Nicholson 1985). In all the other cases, both strategies should lead to equivalent results.

In Table 1, we have compared $|F_o|$ and F_o^2 refinements done with CRYSTALS using, as suggested by the program, a 3-parameters Chebyshev polynomial when refining on $|F_o|$, and the "quasi-statistical" weighting scheme (cf. CRYSTALS manual for further details) when refining on F_o^2 ; 196 outliers were obtained using F_o^2 , and only 10 using $|F_o|$. We cannot choose between $|F_o|$ and F_o^2 refinement on the basis of statistical descriptors. A direct comparison between the residuals of the two refinements is not correct because the probability density function (pdf) of the residual in the $|F_o|$ case is in theory Gaussian, whereas that in the F_o^2 case is not. Durbin-Watson statistics for a ΔF distribution gives nearly equal results (1.926 and 1.924

TABLE 1. Comparison of the results of structure refinements performed with different packages and conditions

Site	x/a	y/b	z/c	ss/ion*	U_{33}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F_o refinement (CRYSTALS) – “Best” model†											
M1	0	0	0	13.126(13)	0.0054	473(3)	639(4)	506(3)	–109(2)	–60(3)	–15(2)
M2	0.9901(1)	0.2776(1)	¼	13.010(13)	0.0055	618(4)	431(4)	596(4)	0	0	16(2)
T	0.4267(1)	0.0943(1)	¼	0.67(5)	0.0038	309(2)	374(2)	447(2)	0	0	11(2)
O1	0.7659(1)	0.0917(1)	¼	0.38(5)	0.0054	361(4)	651(5)	605(5)	0	0	13(4)
O2	0.2208(1)	0.4475(1)	¼	0.20(4)	0.0053	551(4)	385(5)	647(5)	0	0	–8(4)
O3	0.2781(1)	0.1633(1)	0.0333(1)	0.36(3)	0.0058	545(3)	620(4)	573(3)	156(3)	–15(3)	28(3)
F_o^2 refinement (CRYSTALS)‡											
M1	0	0	0	13.127(13)	0.0054	473(4)	632(3)	511(3)	–107(2)	–65(2)	18(2)
M2	0.9901(1)	0.2776(1)	¼	12.995(13)	0.0055	619(3)	422(3)	595(3)	0	0	10(2)
T	0.4267(1)	0.0943(1)	¼	0.65(3)	0.0038	308(2)	375(2)	452(2)	0	0	14(2)
O1	0.7661(1)	0.0918(1)	¼	0.41(5)	0.0054	357(4)	658(5)	599(6)	0	0	23(4)
O2	0.2208(1)	0.4475(1)	¼	0.15(4)	0.0053	554(5)	388(4)	655(5)	0	0	2(4)
O3	0.2781(1)	0.1633(1)	0.0333(1)	0.40(3)	0.0058	547(3)	624(3)	565(3)	150(3)	–20(3)	32(3)
F_o^2 refinement (SHELX-97)§											
M1	0	0	0	13.144(13)	0.0054	476(4)	643(4)	511(4)	–110(3)	–64(3)	–14(3)
M2	0.9901(1)	0.2776(1)	¼	13.020(13)	0.0055	621(4)	433(4)	599(4)	0	0	14(3)
T	0.4267(1)	0.0943(1)	¼	0.67(4)	0.0038	314(3)	379(3)	450(3)	0	0	10(2)
O1	0.7661(1)	0.0917(1)	¼	0.23(4)	0.0054	361(5)	649(7)	603(6)	0	0	11(5)
O2	0.2208(1)	0.4475(1)	¼	0.26(4)	0.0053	554(5)	385(6)	645(6)	0	0	–10(5)
O3	0.2781(1)	0.1633(1)	0.0333(1)	0.33(4)	0.0058	543(4)	619(5)	573(4)	154(4)	–15(4)	29(4)

Note: The anisotropic displacement parameter is of the form $\exp[-2\pi^2(h^2 \cdot a^{*2} \cdot U_{11} + k^2 \cdot b^{*2} \cdot U_{22} + l^2 \cdot c^{*2} \cdot U_{33} + 2 k \cdot l \cdot b^* \cdot c^* \cdot U_{23} + 2 h \cdot l \cdot a^* \cdot c^* \cdot U_{13} + 2 h \cdot k \cdot a^* \cdot b^* \cdot U_{12})]$; $U_i \times 10^3$ in electrons per formula unit.

* M1, M2: refined site-scatterings; T, O1, O2, O3: refined occupancies of neutral vs. fully ionized scattering-curves.

† $R_{\text{obs}} = 2.4\%$; $R_w = 1.8\%$; GooF = 1.10; overall scale factor = 3.132(3); secondary extinction (Larson 1969) = 51(3).

‡ $R_{\text{obs}} = 2.4\%$; $R_w = 1.8\%$; GooF = 1.06; overall scale factor = 3.130(13); secondary extinction (Larson 1969) = 53(2).

§ $R_{\text{obs}} = 2.5\%$; $R_w = 4.8\%$; GooF = 1.14; overall scale factor = 3.135(4); secondary extinction = 0.1(4).

for the $|F_o|$ and the F_o^2 refinements, respectively, to be compared with a theoretical value of 2). The highest ΔF values among the “deleted residuals”¹ are 0.50 and 0.83, respectively.

The SHELX-97 suite also allows weighting as a function of a combination of F_o^2 and F_c^2 and restraining the Goodness of Fit (GooF) to values ≥ 1 . The largest differences from the model obtained with CRYSTALS (although still within e.s.d.) are in the estimates of the components of the atom-displacement parameters (which have the largest e.s.d.), in the site scattering, and in the ionization state. If the number of outliers is the only significant criterion, $|F_o|$ refinement should be preferred for the data set discussed in the present work. The model of Table 1a was thus chosen as “best” model of reference for further work.

When a Gaussian (i.e., $1/\sigma^2$) weighting scheme fails to flatten the residuals during crystallographic refinement, the least-squares minimization is inadequate, and robust-resistant procedures should be used.

A comprehensive review of the effects of using different weighting schemes in the refinement of organic and inorganic structures has been recently provided by Spagna and Camalli (1999). They concluded that the best results can be generally obtained with weighting schemes providing flattening of the outliers as a function of $\sin\theta/\lambda$, and the second best with the Chebyshev polynomials provided by CRYSTALS. We are discussing below the results obtained on olivine by using: (1) unit weights (e.g., ORFLS); (2) Chebyshev polynomials (CRYS-

TALS; Carruthers and Watkin 1979); (3) robust-resistant weights based on Chebyshev polynomials (CRYSTALS); (4) quasi-statistical weights on F_o^2 ; (5) the SHELX weighting scheme (Wilson 1976).

In cases 2 and 3, the reflections are grouped in an appropriate number of intervals, and the sum $\Sigma|F_o|$ and $\Sigma|F_c|$ are calculated for each interval. A 3rd, 4th, 5th-order polynomial $P(<|F_o|>)$ (in our case, the Chebyshev one) is calculated to reproduce $\Sigma\Delta F$. The j^{th} -weight w_j for the j^{th} -reflection is $w_j = 1/P(<|F_o|>)$. Figures 3a and 3b show the average values of $\log(w\Delta F^2)$ obtained in F_o and $\sin\theta/\lambda$ intervals after $|F_o|$ refinement with the robust-resistant weights available in CRYSTALS (black circles). They are compared with the averages of the residuals obtained from unit-weights refinement (open circles) to show the effectiveness of weighting scheme no. 3; systematic trends are no longer present, and the residuals are statistically satisfactory.

Comparative residual analysis showed that the best results during F_o^2 refinement with CRYSTALS are obtained with weights based on Chebyshev polynomials, whereas robust-resistant weights should be used during $|F_o|$ refinement.

Weighting as a function of $\sin\theta/\lambda$ should be used in our opinion only when trends in the residuals as a function of resolution are clearly present. In all the other cases, care must be taken before introducing a $\sin\theta/\lambda$ -dependent parameter in the weighting formula. In fact, this may reduce the information present in high-resolution data.

Systematic truncation of the data

Some of the available crystallographic least-squares packages [e.g., CRYSTALS and SIR97 (Altomare et al. 1999)] automatically set the threshold value to 3 for rejecting reflections

¹The deleted residual is the (normalized) residual value calculated for an observation not included in the calculation; it should be closest to zero.

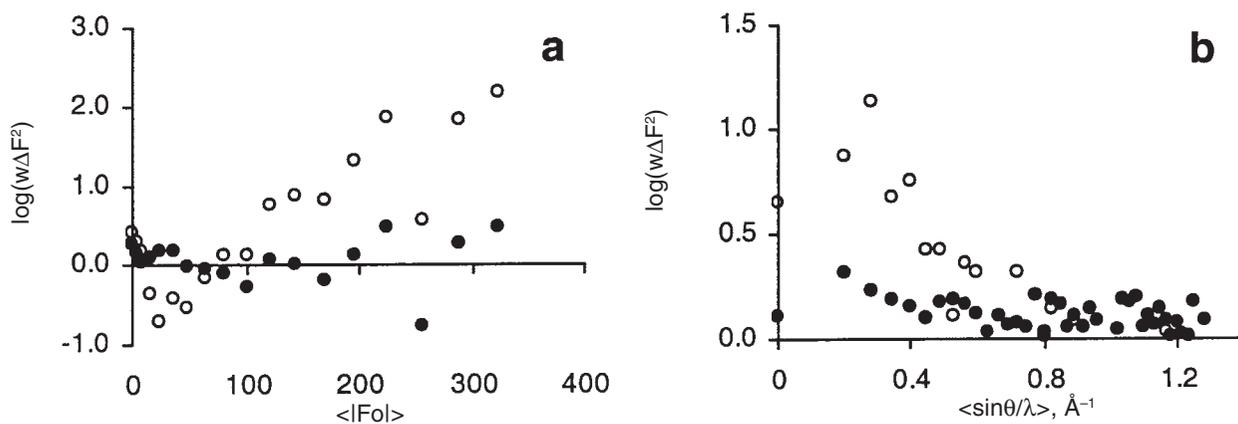


FIGURE 3. Residual analysis of the $|F_0|$ refinements done with the robust-resistant weighting scheme based on Chebyshev polynomials in CRYSTALS (black circles) and with unit weights (open circles). The values of the ordinate are averaged over proper $|F_0|$ and $\sin\theta/\lambda$ intervals, the latter having nearly the same number of reflection; thus the ranges of the ordinate are not the same in the two plots.

on the basis of their I/σ_I (or F_0/σ_{F_0}) ratio; however, these packages are designed for organic molecules, in which the weakest reflections are likely to bias the refinement. Whitacker (1994) discussed the many problems that might be encountered when truncating the data during structure refinement; again, that work deals with organic pigments, which surely have a diffraction behavior worse than that of minerals. In our case study, 85% of the reflections have $F_0/\sigma_{F_0} \geq 3$, and omission of the 241 reflections with $F_0/\sigma_{F_0} < 1$ yields to the results reported in Table 2a. The improvement in the figures of merit is significant: GooF lowers to 1.0002, the R factor for the observed reflections decreases as expected from the reduced number of reflections, and the weighted R_w factor increases from 1.8 to 2.4% thus exceeding R_w , suggesting a better evaluation of the weights. In fact, the normal probability plot of the $1/\sigma$ -weighted residuals is ideally a straight line with slope 1, so that a slope smaller than 1 implies a general overestimation of the individual σ associated to each reflection (Hamilton 1974). The number of outliers, for which the weight is automatically set to zero, decreases to 8. The total octahedral site-scattering lowers to 26.122 epfu (from 26.136 epfu), although within e.s.d.; however, the chemical analysis on the crystals accounts for 26.114(100) epfu. There is some evidence that the reflections with $F_0/\sigma_{F_0} < 1$ may introduce some bias, but the differences are not really critical for this data set (they might be for other data sets). Because the importance (leverage) of the weak reflections is further reduced by squaring, their truncation is less critical (although still potentially dangerous) when refining on F_0^2 .

To test the effects on the refinement results caused by the resolution of the diffraction data, we refined the subset with $\sin\theta/\lambda \leq 0.7$ ($\theta = 30^\circ$ MoK α) (Table 2b), the resolution more often used in crystallographic analysis. As expected, the changes are far more significant, and larger than e.s.d., especially as far as the atom-displacement parameters and the ionization state are concerned. Site-scattering estimates diverge by -0.079 epfu at M1 and -0.016 epfu at M2 (-0.006 and -0.001 in terms of Mg occupancies), thus significantly affecting kinetic calculations.

LEVERAGE ANALYSIS

The theory of leverage analysis and its implication in the structure refinement of minerals were reported and discussed in Merli et al. (2000). In essence, given \mathbf{W} the diagonal weight matrix and \mathbf{A} the matrix representing the model, we can define a matrix $\mathbf{Z} = \mathbf{W}\mathbf{A}$; \mathbf{Z} has dimensions $n \times p$, [n being the number of observations (i.e., the reflections) and p the number of parameters in the model (i.e., the refined variables)]. Then we can define a $n \times n$ matrix $\mathbf{P} = \mathbf{Z}(\mathbf{Z}^T\mathbf{Z})^{-1}\mathbf{Z}^T$, the so-called “projection matrix”, which has the following properties: (1) $P_{ij} = P_{ji}$; (2) trace (\mathbf{P}) = p ; (3) $0 \leq P_{ii} \leq 1$, (4) $\langle P_{ii} \rangle = p/n$. The leverage of the i^{th} reflection is defined as the diagonal element P_{ii} of the matrix \mathbf{P} , and represents the rate of variation of the calculated value of the variable.

The “best” model reported in Table 1a was used as input for a locally written full-matrix least-squares routine for the ORFLS program that allowed us to store the \mathbf{W} and \mathbf{A} arrays and to carry out leverage analysis. ORFLS only allows refinement of the displacement parameters in terms of B; however, the relation between U and B is such that only the numeric values of the leverage but not their trends are expected to vary.

The leverage of each reflection was calculated with respect to the change of a single variable in a $|F_0|$ least-squares cycle; therefore, the higher its leverage value, the stronger is the contribution of a reflection to the estimate of that single variable. It follows that high-leverage reflections should never be omitted from least-squares refinement, as their omission reduces the available information and may affect the estimate of a variable. If a high-leverage reflection becomes an outlier at convergence (i.e., it has high ΔF values), care must be taken to understand the reason why (experimental errors, inadequate absorption correction, false minimum in the least-squares refinement, incompleteness of the model, etc.). Conversely, if high-leverage reflections are reproduced correctly by the refined model, the corresponding variable is most likely to be correctly estimated, and thus leverage analysis is also a way of validating

TABLE 2. Results of $|F_o|$ refinements with different procedures for data truncation

Site	x/a	y/b	z/c	ss/ion*	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F_o refinement (CRYSTALS) on the 2491 reflections with $F_o/\sigma_{F_o} \geq 1$†											
M1	0	0	0	13.120(13)	0.0054	474(3)	639(4)	509(3)	-110(2)	-61(3)	-14(2)
M2	0.9901(1)	0.2776(1)	1/4	13.002(13)	0.0055	618(4)	432(4)	596(4)	0	0	17(2)
T	0.4267(1)	0.0943(1)	1/4	0.67(5)	0.0038	309(2)	374(2)	447(2)	0	0	11(2)
O1	0.7660(1)	0.0917(1)	1/4	0.33(5)	0.0054	361(4)	651(5)	605(5)	0	0	13(4)
O2	0.2208(1)	0.4475(1)	1/4	0.20(4)	0.0053	551(4)	385(5)	647(5)	0	0	-8(4)
O3	0.2781(1)	0.1633(1)	0.0333(1)	0.36(3)	0.0058	545(3)	620(4)	573(3)	156(3)	-15(3)	27(3)
F_o refinement (CRYSTALS) on the 463 reflections with $\sin\theta/\lambda \leq 0.7 \text{ \AA}^{-1}$‡											
M1	0	0	0	13.047(13)	0.0069	640(20)	805(19)	621(16)	-91(11)	-60(10)	0(2)
M2	0.9904(1)	0.2776(1)	1/4	12.994(13)	0.0073	810(20)	640(20)	728(18)	0	0	13(11)
T	0.4265(1)	0.0943(1)	1/4	0.64(3)	0.0055	480(17)	585(15)	579(15)	0	0	0(9)
O1	0.7664(1)	0.0917(1)	1/4	0.38(5)	0.0075	670(40)	850(30)	720(30)	0	0	0(20)
O2	0.2205(1)	0.4477(1)	1/4	0.30(4)	0.0069	730(30)	610(30)	720(30)	0	0	70(30)
O3	0.2782(1)	0.1632(1)	0.0334(1)	0.40(3)	0.0078	800(20)	800(20)	740(20)	120(17)	-7(20)	27(19)

Note: The anisotropic displacement parameter is of the form $\exp(-2\pi^2 \cdot (h^2 \cdot a^{*2} \cdot U_{11} + k^2 \cdot b^{*2} \cdot U_{22} + l^2 \cdot c^{*2} \cdot U_{33} + 2 \cdot k \cdot l \cdot b^* \cdot c^* \cdot U_{23} + 2 \cdot h \cdot l \cdot a^* \cdot c^* \cdot U_{13} + 2 \cdot h \cdot k \cdot a^* \cdot b^* \cdot U_{12})$; $U_{ij} \times 10^5$.

* M1, M2: refined site-scatterings; T, O1, O2, O3: refined occupancies of neutral vs. fully ionized scattering-curves.

† $R_{obs} = 2.2\%$; $R_w = 2.4\%$; $Goof = 1.00$; overall scale factor = 3.142(4); secondary extinction (Larson 1969) = 55(3).

‡ $R_{obs} = 2.0\%$; $R_w = 1.3\%$; $Goof = 0.94$; overall scale factor = 3.139(11); secondary extinction (Larson 1969) = 61(4).

the results of the structure refinement. It must be underlined that leverage analysis is not a tool for “polishing” bad observations, but is a tool for critically detecting the real outliers of the refinement (that are difficult to recognize otherwise).

All the variables of interest in the structure refinement of olivine have been checked by means of leverage analysis by using the complete data set up to $\theta = 67.5^\circ$; only the most interesting results are discussed in the following. Lists of the 10 reflections with the highest leverages on each variable relevant to the present discussion are reported in Tables 3 and 4. Some of them strongly contribute to the estimate of more than one variable, such that the accuracy in their estimate is strictly correlated. For instance, the 110 reflection has the highest leverage on both the M1 site-scattering and the overall ionization state at the T and O sites; thus the site scattering at M1 cannot be estimated correctly if a wrong model for the ionization has been adopted (e.g., when using scattering curves for the chemical constituents which do not represent their actual ionization state).

Figure 4 shows the leverage of each reflection on the estimate of the site scattering at M1 and M2 plotted as a function of $|F_o|$ and $\sin\theta/\lambda$, respectively. The trends observed for the two sites are strictly analogous. In particular, Figures 4b and 4d show that only diffraction data up to $\sin\theta/\lambda = 0.9 \text{ \AA}^{-1}$ ($\theta = 40^\circ$ for $\text{MoK}\alpha$) allow reliable estimates of the site scattering (which is consistent with Table 2b), and that entire classes of reflections (those with $h + k + l = 2n + 1$, i.e., half of the total reflections) do not contain any information on the site-scattering at M1. This is the reason why the site scattering at M1 is most affected by truncation at $\sin\theta/\lambda = 0.7 \text{ \AA}^{-1}$ (Table 2b).

If we omit the 10 highest-leverage reflections for the site scattering at the M1 site in Table 3c (7 of which have also the highest leverage values on the site scattering at the M2 site; Table 3d), the leverage values of the remaining reflections in the data set are practically unchanged. Thus the information contained in the missing reflections is lost when they are omitted.

The 241 reflections with $F_o/\sigma_{F_o} < 1$ have a mean leverage on

the site scattering at the M1 and M2 sites lower than 10^{-5} ; this explains why the results reported in Table 2a do not significantly differ in terms of their estimate. This conclusion cannot be straightforwardly extended either to other mineral structures or to highest cut-off thresholds.

The highest-leverage reflection on the site scattering at the M1 site is 110, a medium-intensity reflection with $F_o/\sigma_{F_o} = 13$. It is not affected by the Renninger effect, as shown by a constancy of its F_o - F_c agreement before and after applying the correction discussed in the proper section. However, 110 is an outlier in all the $|F_o|$ refinements done in this work. Inspection of the diffracted intensities showed that one of the two collected equivalents was 30% less intense than the other (after correction for absorption and L_p factors), and lowered by 15% the merged value used in the refinement. The results reported in Tables 1–4 were obtained after omission of the weaker equivalent.

When using the data set with the correct 110 intensity, all the outliers in the refinements were low-leverage reflections, independently from the procedure followed (e.g., Tables 1 and 2). The weight assigned to 110 was 0.9 in the whole-data refinement and 1.9 in that done on the reflections with $F_o/\sigma_{F_o} \geq 1$, to be compared with 0 when it was an outlier. In the different trials, the refined site-scattering at M1 varied within the e.s.d.; however, correction of the experimental problems affecting the 110 intensity also guarantees against bad estimates of all the variables correlated with the site scattering at M1.

Figure 5 refers to the estimate of the scale factor and of the secondary extinction coefficient. The analogous plots obtained for garnet and amphibole showed that leverage values on their estimates were comparable (Merli et al. 2000); in olivine, leverage values on the secondary extinction are 10 times those on the scale factor (as far fewer reflections contribute to its estimate), suggesting that a good estimate of the extinction coefficient is very critical.

Figure 6 shows the leverage values on the β_{11} component of the atom displacement parameters at the M1 and M2 sites

TABLE 3. Reflections with the highest leverage (L) on the most important parameters for olivine structure refinement

$h k l$	F_o	σ_{F_o}	F_o/σ_{F_o}	$\sin\theta/\lambda$	L
Overall scale factor					
0 0 4	1170.8	15.8	74	0.33	0.0364
0 6 2	966.4	0.5	1933	0.34	0.0283
2 2 2	784.3	16.5	48	0.29	0.0180
4 0 0	648.3	3.4	191	0.42	0.0139
2 4 0	603.6	3.2	189	0.29	0.0117
1 3 0	628.1	15.0	42	0.18	0.0117
1 1 2	671.5	24.5	27	0.20	0.0116
1 7 0	614.9	7.8	79	0.36	0.0114
3 2 2	583.2	3.2	182	0.37	0.0100
1 4 0	584.6	17.0	34	0.22	0.0094
Secondary extinction coefficient					
0 0 4	1170.8	15.8	74	0.33	0.3678
0 6 2	966.4	0.5	1933	0.34	0.1991
2 2 2	784.3	16.5	48	0.29	0.0866
1 3 0	628.1	15.0	42	0.18	0.0638
1 1 2	671.5	24.5	27	0.20	0.0518
2 4 0	603.6	3.2	189	0.29	0.0275
1 3 1	550.8	21.7	25	0.20	0.0261
1 4 0	548.6	16.9	32	0.22	0.0251
4 0 0	648.3	3.4	191	0.42	0.0197
1 7 0	614.9	7.8	79	0.36	0.0161
Site scattering at the M1 site					
1 1 0	54.5	2.1	26	0.12	0.0161
0 2 0	83.7	0.3	279	0.10	0.0128
0 4 0	31.2	0.5	62	0.20	0.0124
0 2 2	109.9	0.4	275	0.19	0.0123
2 0 0	109.8	0.4	274	0.21	0.0116
2 2 0	52.7	1.5	35	0.23	0.0108
0 0 2	445.3	0.3	1484	0.17	0.0098
1 3 2	207.1	0.4	518	0.25	0.0096
0 4 2	212.3	0.5	424	0.26	0.0091
2 0 2	157.9	3.0	53	0.27	0.0090
Site scattering at the M2 site					
1 1 1	208.4	1.0	208	0.14	0.0142
0 2 0	283.7	0.3	946	0.10	0.0123
2 0 0	109.8	0.4	274	0.21	0.0122
0 2 2	109.9	0.4	275	0.19	0.0118
0 0 2	445.3	0.3	1484	0.17	0.0106
2 2 0	52.7	1.5	35	0.23	0.0101
2 0 2	157.9	3.0	53	0.27	0.0094
1 1 3	216.0	3.7	58	0.28	0.0088
0 4 0	31.2	0.5	62	0.20	0.0080
3 1 1	243.0	1.6	152	0.33	0.0066
overall ionization state at the T and O sites					
1 0 1	282.0	6.0	47	0.13	0.5081
0 2 1	421.3	0.3	1404	0.13	0.4769
1 2 0	247.0	2.6	95	0.14	0.4515
2 0 0	109.8	0.4	274	0.21	0.4002
0 2 0	283.7	0.3	946	0.10	0.3499
1 1 0	54.5	2.1	26	0.12	0.3095
0 0 2	445.3	0.3	1484	0.17	0.3081
0 2 2	109.9	0.4	275	0.19	0.1596
1 2 2	498.7	9.4	53	0.22	0.1444

TABLE 4. Reflections with the highest leverage (L) on the diagonal elements of the atom displacement tensors at the M1 and M2 sites in olivine

$h k l$	F_o	σ_{F_o}	F_o/σ_{F_o}	$\sin\theta/\lambda$	L
β_{11} at the M1 site					
10 0 0	85.1	1.0	85	1.05	0.0069
11 1 0	44.2	1.5	29	1.15	0.0069
9 1 0	53.7	0.9	60	0.94	0.0069
10 2 0	16.5	4.1	4	1.05	0.0068
12 0 0	66.7	1.7	39	1.26	0.0067
11 3 0	32.3	1.9	17	1.16	0.0067
10 0 2	45.0	0.9	50	1.06	0.0067
8 0 0	107.7	0.7	154	0.84	0.0066
β_{11} at the M2 site					
6 0 0	35.1	0.8	44	0.60	0.0057
8 0 0	107.7	0.7	153	0.84	0.0055
7 1 1	146.1	0.8	192	0.74	0.0054
8 0 2	82.5	1.9	43	0.85	0.0051
6 0 2	199.4	1.1	181	0.65	0.0050
6 2 0	52.8	2.4	22	0.63	0.0049
9 1 1	90.6	1.9	48	0.95	0.0048
8 2 0	20.5	8.5	2	0.84	0.0048
β_{22} at the M1 site					
0 16 0	202.9	0.9	225	0.78	0.0067
0 18 0	201.1	0.9	223	0.88	0.0066
1 17 0	124.8	1.4	89	0.89	0.0065
0 20 0	96.0	1.0	96	0.97	0.0065
0 14 0	104.5	0.8	131	0.68	0.0065
1 19 0	16.1	1.4	11	0.93	0.0065
0 18 2	65.0	1.0	65	0.89	0.0063
1 21 0	24.8	1.3	19	1.03	0.0063
β_{22} at the M2 site					
0 18 0	201.1	0.9	223	0.88	0.0074
0 26 1	48.7	0.8	61	1.27	0.0073
1 19 1	131.8	2.1	63	0.94	0.0071
0 18 2	65.0	1.0	65	0.89	0.0070
0 20 0	96.0	1.0	96	0.97	0.0070
1 17 1	30.6	1.0	31	0.84	0.0067
2 26 1	39.6	0.7	57	1.29	0.0067
2 18 0	42.9	2.3	19	0.91	0.0066
β_{33} at the M1 site					
0 0 12	193.9	1.0	194	1.00	0.0071
0 0 14	133.1	0.9	148	1.16	0.0071
0 2 12	95.2	1.0	95	1.01	0.0071
1 1 12	12.7	5.9	2	1.01	0.0070
0 2 14	55.6	1.0	56	1.17	0.0070
1 1 14	90.1	0.7	129	1.17	0.0070
0 0 10	220.1	0.9	245	0.83	0.0068
0 2 10	91.8	1.0	92	0.84	0.0068
β_{33} at the M2 site					
0 0 10	220.1	0.9	245	0.83	0.0069
0 0 12	193.9	1.0	194	1.00	0.0068
1 1 11	34.1	1.2	28	0.93	0.0066
1 1 9	24.8	1.3	19	0.76	0.0064
0 0 14	133.1	0.9	148	1.17	0.0064
1 1 13	14.7	2.4	6	1.09	0.0063
2 0 12	139.0	0.7	199	1.02	0.0062
2 0 10	57.4	1.1	52	0.86	0.0061

plotted as a function of $\sin\theta/\lambda$; the strips in Figure 6a are related to classes of reflections differing by the value of h (1, 2, ..., n). The importance of high-resolution data is evident from Figure 6 and Table 4, in which most highest-leverage reflections occur at $\sin\theta/\lambda \geq 0.80 \text{ \AA}^{-1}$, and is confirmed for all the components of the anisotropic displacement parameters at all the structural sites. Accordingly, inspection of Table 2b shows that the e.s.d. of the components of the

anisotropic displacement factors obtained after refinement limited to $\sin\theta/\lambda \leq 0.70 \text{ \AA}^{-1}$ are up to ten times those obtained from the whole data set. Similar results were obtained for garnet in Merli et al. (2000).

DISCUSSION

Several useful suggestions for the best procedure to be adopted in a standard structure refinement of a mineral family

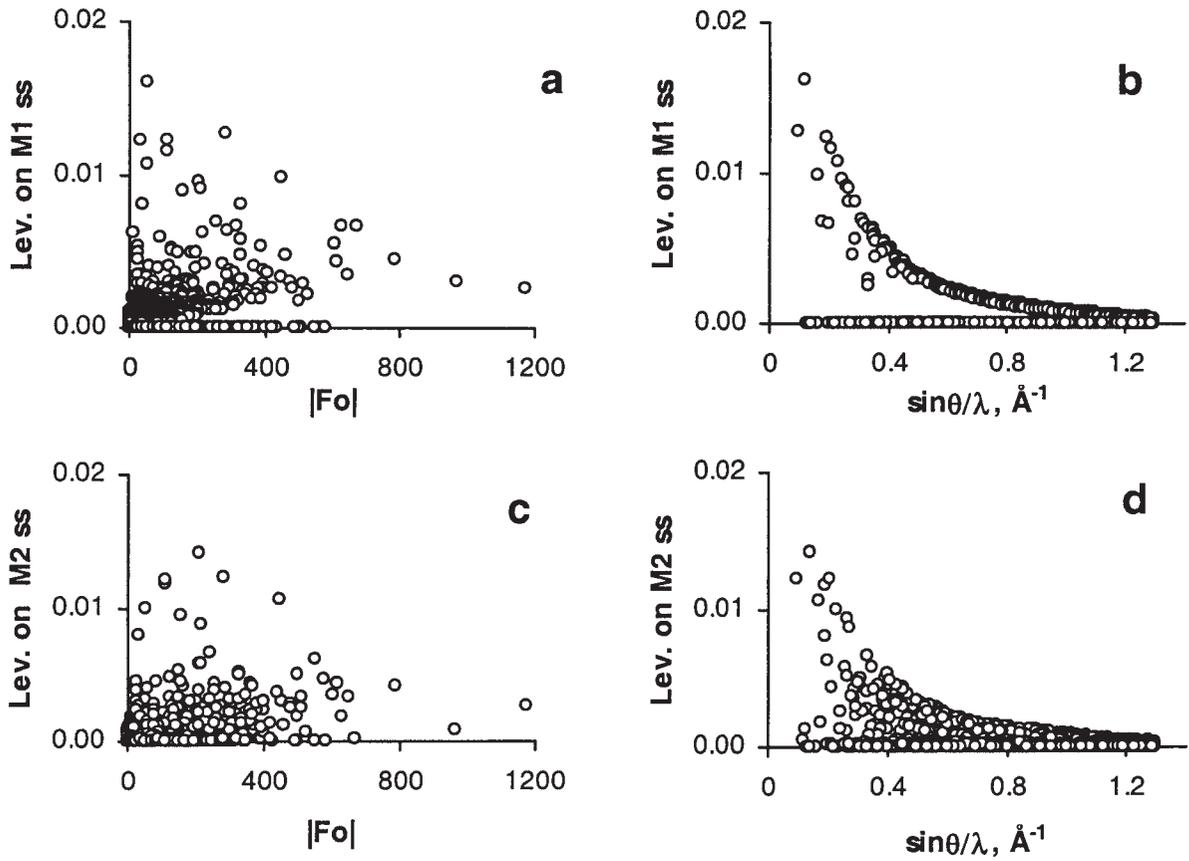


FIGURE 4. Analysis of the leverage of each reflection in the data set on the estimate of the site scattering at the M1 (a and b) and M2 (c and d) sites.

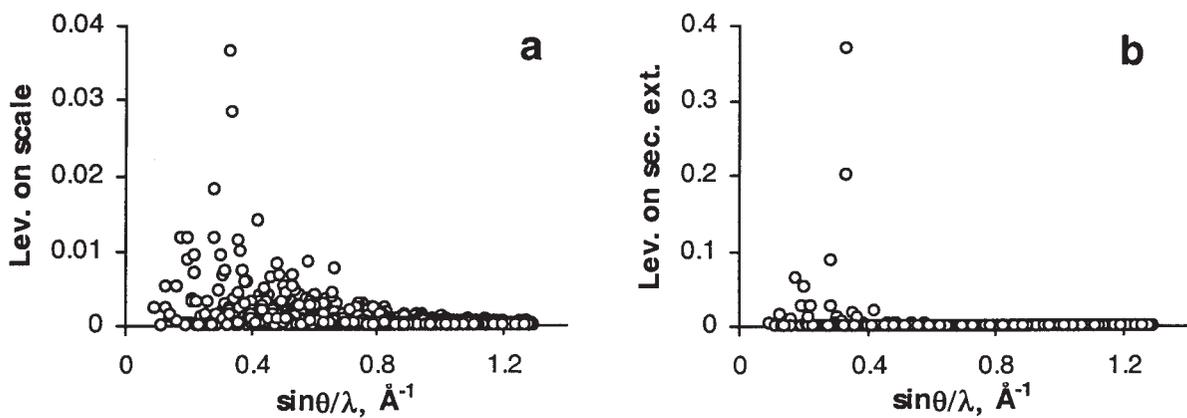


FIGURE 5. Analysis of the leverage of each reflection in the data set on the estimate of the scale factor (a) and of the secondary extinction coefficient (b) as a function of $\sin\theta/\lambda$.

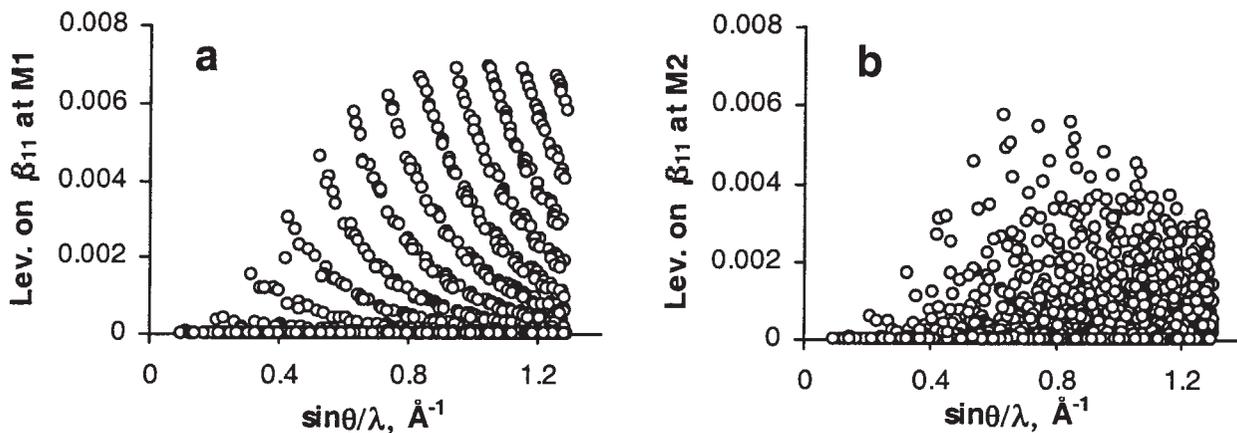


FIGURE 6. Analysis of the leverage of each reflection in the data set on the estimate of the β_{11} component of the displacement factor at the M1 (a) and the M2 (b) sites as a function of $\sin\theta/\lambda$.

can be obtained by combining leverage analysis with a careful evaluation of the results obtained by using different refinement procedures. This is particularly critical when highly reliable results are needed for geothermometric and geospeedometric purposes. In the case of olivine, the present work suggests the use of high-resolution data ($\theta \geq 45^\circ \text{ MoK}\alpha$) which should be refined with robust-resistant weights on $|F_o|$ with a package which allows reliable correction for secondary extinction.

Tests done under the best conditions on the high-resolution high-quality set of data of the present work show that the e.s.d. on the refined site-scattering is never lower than 0.013 electrons, which means one on the third digit on site occupancies. This value is actually related to the precision of the estimate; its accuracy is more difficult to be evaluated, even if the presence of an internal standard in structure refinement procedures (i.e., the site scattering at all the sites where chemical substitutions do not occur) suggests that X-ray crystallography is also highly accurate. However, a precision on the fourth digit, as it is sometimes claimed, is hard to believe and may result from excessive "polishing" of the data that may introduce systematic bias in the estimates.

Electron-microprobe analyses may suffer from a series of problems related to the use of inappropriate standards (e.g., matrix effects), infrequent measurement of the standards, and variable experimental conditions during the analysis. They can also be affected by sample inhomogeneity or zoning, which both could bias the results, and by hardly detectable or undetectable elements (e.g., those with atomic number < 6) whose omission would significantly affect unit-formula calculation; in contrast, the refined site-scattering takes into account all the chemical elements that are ordered in the mineral matrix (inclusions do not significantly contribute to the measured diffraction) and is averaged over the entire crystal under examination.

Thus introducing a restraint derived from chemical analysis in the structure refinement is potentially dangerous if the estimated errors are not appropriate; they can bias the results

by affecting both the minimization function at the basis of the process and the statistical tests on the results. The use of geometrical restraints in "badly diffracting" compounds such organic materials is a completely different matter; it is certainly both far less dangerous and useful in improving the results. Geometrical restraints (to interatomic distances) may be also useful in the structure refinement of minerals in the presence of hydrogen and/or split sites.

Care should also be paid when the results of the structure refinement are combined with those of the electron-microprobe analyses, and the differences between the two estimates are minimized before doing thermodynamic and kinetic modeling. Obviously, chemical analyses are valuable to detect the presence (and to quantify the amounts) of minor substituents that cannot be identified by structure refinement. Their contribution must be subtracted from the total site-scattering to obtain reliable estimates of site occupancies of the substituents relevant to geothermobarometry and to kinetic and thermodynamic modeling, which are usually solely Fe^{2+} and Mg.

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