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FAST DETERMINATION OF THE CRYSTAL-CHEMICAL COMPOSITION OF Pbca ORTHOPYROXENES AND P2/n CLINOPYROXENES BY MEANS OF THE MEASUREMENT OF THE X-RAY DIFFRACTED INTENSITIES OF FEW REFLECTIONS

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RIASSUNTO. — Lo studio tramite diffrattometria a cristallo singolo delle cinetiche dei fenomeni di ordine-disordine nei minerali delle rocce ha reso sempre più indispensabile una rapida ed accurata determinazione di alcuni parametri cristallochimici, necessari per seguire l'andamento della transizione. Questa esigenza era del resto già avvertita nell'ambito dello studio cristallochimico degli stessi minerali, per evitare di sprecare tempo di diffrattometro e di calcolo su cristalli simili a quelli già studiati. A questo scopo, mediante il procedimento già proposto per i clinoanfiboli, sono stati messi a punto due programmi FORTRAN, uno (ORTHOPYR) per gli ortopirosseni e uno (CLINOPYR) per le onfaciti. Questi programmi, mediante la misura rispettivamente di 133 e 116 riflessi, particolarmente sensibili alle variazioni di composizione, permettono di calcolare con un alto livello di attendibilità le distanze medie e il numero atomico medio di ogni sito cationico, senza ricorrere ad un raffinamento con dati completi. I due programmi, che si riducono al calcolo di combinazioni lineari contenenti non più di 40 termini ciascuna (ogni termine consta di un'intensità misurata moltiplicata per un opportuno coefficiente), possono essere utilizzati su un qualsiasi « personal computer » o essere direttamente inseriti nel « software » di controllo del diffrattometro.

ABSTRACT. — By applying the same principle used for the clino-amphiboles, two FORTRAN programs have been set up, one for ortho- (ORTHOPYR) and one for P2/n clinopyroxenes (CLINOPYR). The measurement of 133 and 116 reflections respectively, which are particularly sensitive to the crystal-chemical variations, allows to calculate the mean bond distances and the mean atomic number of the octahedral sites. The great accuracy of the crystal-chemical results allows to avoid complete X-ray data collection and refinement. The two programs, which consist in the calculation of linear combinations of no more than 40 terms, may be performed on any personal computer or be inserted in the standard software of a single-crystal diffractometer.

Introduction

The crystal-chemical investigation of the rock-forming minerals — which has been the main research program at the Centro di Studio per la Cristallografia Strutturale of Pavia in the last five years — yielded a great deal of X-ray crystal structure refinements of amphiboles, orthopyroxenes and clinopyroxenes. The procedures of data collection, data reduction and least-squares refinement (UNGARETTI, 1980) have been optimized so that highly accurate crystal-chemical information is always achieved: the final discrepancy indices are usually between 1.2 and 2.0 %, while the e.s.d. on the calculated bond lengths are near $\pm$ 0.001 Å.

Recently, a new kind of experiments has been set up, in order to study the kinetics of the order-disorder phenomena in omphacites and in orthopyroxenes: this implies that the X-ray structure determination must be worked out at first on the natural specimen and then on the same crystal after annealing it for different times. The whole sequence has to be carried out for different temperatures and for crystals of different composition. Tens of X-ray data collections and structure refinements are the basis of this

kind of investigation and this is a time consuming and expensive procedure. On the other hand, only the accurate determination of the mean atomic number in the octahedral sites is needed to follow the order-disorder transformation. If a check of the self-consistency of the results is wanted, a limited number of geometric parameters, like the mean distances between the central atom and the coordinated oxygens has to be calculated. Moreover the Si-O non bridging mean distance is useful to evaluate the Al^{IV} content.

Previous experiences on amphiboles of wide-ranging crystal-chemical compositions have shown that the various isomorphous substitutions occurring in the amphibole structure determine large intensity changes only in a small number of reflections (CANNILLO and UNGARETTI, 1983). The intensities of the reflections which are more sensitive to the chemical composition were therefore correlated, by using a stepwise multiple regression procedure, to the geometric and chemical parameters which are needed to calculate the crystal-chemical formula of an amphibole. A similar approach has been applied to orthopyroxenes and to primitive omphacites, in order to follow the order-disorder transformation without performing complete X-ray data collections and least-squares refinements.

Method

The first step was to recognize the reflections which are more sensitive to the site population changes and those which are quite constant and can therefore be used to put the intensities on absolute scale. In orthopyroxenes — unlike amphiboles — all the reflections are very sensitive to crystal-chemical variations. Because of the lacking of individual reflections with constant intensities, it has been looked for sets of a small number of reflections in which the sum of the intensities was constant. To get this goal it was necessary to sum up six reflections selected among the 190 more intense ones. Their indices are reported in table 1. The complete diffraction data of 48 orthopyroxenes were then compared, and 250 strong reflections with the largest intensity changes were selected among the 1400 independent reflections in the ϑ range 2°-30°. A stepwise multiple regression procedure was then applied to these 250 reflections, in order to correlate the changes in the intensities and the unit-cell parameters with the number of electrons in the M1 and M2 sites, the mean <M1-O>, <M2-O>, <SiA-O>, <SiB-O>, and $<SiB\text{-}O>_{n.br.}$ distances.

Because of the need of accurate determination of these parameters, which could substitute for the results of a complete X-ray crystal-structure refinement, a great care was taken in checking the reliability of the results. Therefore the number of the terms in the final linear combinations was enlarged with respect to the case of amphiboles. The final set of equations, which allows to calculate the crystal-chemical parameters is reported in table 1, together with the multiple correlation coefficients: 133 independent reflections were used. An evaluation of the accuracy of the results obtained in this way is reported in fig. 1, where the calculated values are compared with those obtained from the complete X-ray crystal-structure refinements. Obviously, these plots refer to crystals which were not used for the calculation of the coefficients of the equations reported in table 1.

The same procedure has been followed for the P2/n clinopyroxenes. In this case the intensity data collected from 37 crystals were used, each set of data consisting of around 1500 independent reflections in the ϑ range 2°-30°. Because of the intrinsic weakness of the $h+k$ odd reflections, the search for sensitive reflections was carried out separately for the $h+k$ odd and $h+k$ even sets: at the end, for the stepwise multiple regression procedure the 134 and 104 strongest reflections with the largest changes in intensities were taken into consideration. The scale factor was calculated in the same way as in orthopyroxenes using the 77 strongest reflections with $h+k$ even: a combination of the intensities of only four reflections was found to be sufficiently accurate.

The final equations for the calculation of crystal-chemical parameters in P2/n clinopyroxenes are reported in table 2: 116 independent reflections were used. The range of chemical variation in omphacites is

TABLE 1

Regression equations relating the intensities (on absolute scale) of 133 reflections and the unit-cell dimensions to the crystal-chemical parameters in orthopyroxenes

K = 24164 / [(5 1 4) + (7 1 4) + (1 5 4) + (4 3 1) + (4 3 0) + (16 1 2)]

<M1-O> = 0.16089 b − 1.39170 (8 1 1) + 0.70369 (0 4 3) − 1.13122 (4 1 2) + 0.14192 (4 3 0)
+ 0.11062 a − 0.95657 (10 3 3) − 0.77705 (2 4 1) − 0.69543 (1 9 3) + 0.41095 (16 2 0)
+ 1.42827 (15 3 3) + 1.02489 (10 5 0) + 0.74663 (11 6 2) − 2.00235 (5 11 2) − 0.62872 (8 5 2)
− 1.11705 (1 8 3) − 1.35511 R = 0.999

<M2-O> = 5.16549 (7 5 1) + 0.21353 c − 11.24868 (4 0 2) + 0.14688 (2 0 2) − 4.68590 (10 3 3)
+ 1.79313 (8 4 0) − 3.43249 (2 3 0) + 0.46890 (14 3 3) − 6.71501 (4 8 1) + 2.84994 (15 8 1)
+ 8.47788 (1 8 3) − 3.00170 (1 6 6) + 5.82017 (16 8 1) − 0.03993 (0 6 0) − 0.14445 (3 0 2)
+ 4.40718 (13 2 1) − 2.09058 (7 2 3) − 1.58156 (12 6 0) + 1.38321 (5 6 2) + 1.30712 (6 11 0)
+ 0.92684 (13 0 6) + 1.05594 R = 0.999

<SiA-O> = 0.13526 (0 2 0) − 0.02317 (2 0 2) + 0.76803 (4 3 0) − 0.01392 (4 1 1) + 1.23161 (8 1 2)
− 0.36994 (12 5 2) + 1.08364 (0 0 2) + 0.16723 (1 0 4) + 1.39931 (1 4 3) + 0.31695 (4 3 1)
− 0.05857 (1 3 3) + 0.81051 (4 3 2) − 0.19221 (3 2 1) + 0.00054 Vol − 1.94684 (6 5 4)
+ 2.13317 (10 9 1) − 1.73098 (16 2 0) + 1.00990 (3 5 3) + 0.60792 (10 5 4) + 1.65660 (6 5 1)
− 0.30701 (4 2 5) − 0.85544 (4 6 4) − 1.02560 (5 4 1) + 0.63111 (4 4 1) + 0.39926 (9 6 2)
+ 1.46357 (6 1 5) + 0.21157 (0 4 3) − 1.08672 (5 3 2) − 0.07282 (1 3 1) + 1.15852
R = 0.998

<SiB-O> = 3.00001 (4 0 2) − 0.10904 (4 1 1) + 0.71044 (8 1 1) + 2.87822 (3 4 2) − 0.23817 (2 3 0)
− 1.23604 (1 1 4) + 2.32982 (15 2 2) − 0.62669 (21 3 3) + 1.67730 (6 2 2) − 0.41479 (20 0 0)
+ 0.88326 (4 8 1) − 1.30035 (1 5 6) + 1.32072 (4 8 5) − 0.16450 (12 3 1) + 0.33049 (4 3 0)
− 0.38886 (8 5 2) + 1.62941 R = 0.998

$<SiB\text{-}O>_{n.b.}$ = 1.59848 (4 0 2) − 0.23286 (10 3 3) − 0.03435 b + 3.95917 (19 0 2) + 0.08364 (4 1 2)
− 6.06881 (18 3 1) + 5.40567 (18 5 0) + 0.51765 (6 0 0) − 0.40348 (20 0 0) + 1.34785 (8 3 1)
− 0.34911 (2 2 1) + 2.95562 (8 1 1) − 0.59591 (10 5 0) + 0.76082 (17 3 1) + 0.10460 (2 0 2)
− 1.15481 (14 5 1) + 0.53275 (20 6 0) − 2.36127 (13 2 3) + 3.57395 (3 4 2) − 0.44693 (0 2 1)
− 2.31806 (2 3 0) + 1.60519 (6 5 1) − 1.21055 (9 3 5) + 0.53327 (8 4 0) + 1.89869
R = 0.998

m.a.n. M1 =−153.79370 (12 2 1) − 80.74670 (10 1 0) − 15.59435 (4 2 1) − 61.49474 (5 1 2) − 25.44170 (8 5 2)
+275.47409 (9 1 2) + 16.95392 (0 12 0) + 67.05479 (3 5 2) +689.96737 (11 2 1) + 15.09359 (6 1 0)
− 30.03447 (5 0 2) + 87.29194 (12 2 3) + 92.42854 (9 0 2) −266.30766 (10 7 0) +140.85480 (16 4 0)
−323.70274 (10 5 0) −189.70334 (7 1 1) + 35.27938 (5 2 1) −140.95720 (15 3 3) +533.24409 (9 2 5)
− 77.62559 (6 3 0) + 40.50359 (1 0 4) +218.78689 (10 1 3) + 6.86971 (2 1 0) −179.51058 (5 3 5)
+ 66.49333 (5 5 2) − 62.50048 (12 0 4) − 92.83154 (4 2 5) +203.89357 (14 5 1) + 45.81000 (2 2 7)
− 4.30077 (0 2 3) + 37.62297 (2 4 1) +135.46146 (2 1 4) − 9.43659 (4 0 4) − 9.85046 (13 3 3)
+ 63.56205 (7 3 5) − 4.17525 (2 3 3) + 13.33078 R = 0.999

m.a.n. M2 = 79.82343 (2 5 1) −116.94017 (10 3 3) + 32.86251 (9 2 2) + 1.80444 (5 1 1) − 31.63620 (10 7 0)
− 63.30876 (0 2 0) + 28.64876 (6 5 1) +229.89626 (17 1 3) +146.50190 (7 2 2) +617.25873 (10 5 3)
−136.19481 (14 9 3) + 85.48540 (5 5 1) +294.59559 (12 8 3) +179.32641 (15 0 2) −193.44464 (4 8 5)
+101.70856 (3 1 3) −258.97361 (22 3 1) +113.49328 (1 5 6) +440.24949 (21 3 1) −188.50345 (10 5 0)
+ 81.69610 (4 4 0) +252.46422 (6 2 2) −107.10900 (23 0 2) +180.94991 (11 2 1) − 52.19146 (8 1 2)
−435.88879 (6 1 5) +140.99054 (3 5 3) + 87.08704 (4 2 5) −133.92098 (2 8 1) − 26.23933 (7 0 6)
−228.94945 (9 0 4) − 71.91368 (2 2 7) − 15.70076 (10 3 5) − 48.51255 (10 5 4) − 35.50479 (0 8 3)
+132.13412 (7 8 1) − 35.07591 (7 1 1) + 54.91605 (16 2 0) + 34.32759 (7 8 3) + 17.63304 (21 3 3)
+ 13.17188 R = 0.999

(*hkl*) means intensity of the *hkl* reflection. *K* is the multiplier to put the intensities on the absolute scale.

rather small (from roughly $Jd_{0.40}Di_{0.60}$ to $Jd_{0.60}Di_{0.40}$, disregarding few percents of acmite). Thus plots like those showed in fig. 1 are not useful to monitor the accuracy

TABLE 2

Regression equations relating the intensities (on absolute scale) of 116 reflections and the unit-cell dimensions to the crystal-chemical parameters in P2/n clinopyroxenes

K = 10492 / [(-3 1 5) + (-5 3 5) + (7 1 0) + (3 1 4)]

<M11-O> = 0.11329 (-2 1 3) - 0.02993 β - 0.26780 (-1 6 4) + 0.00746 (-2 8 3) - 0.01665 (-1 9 3)
+ 0.01711 (-2 3 1) + 0.20810 b - 0.14593 (0 7 1) - 0.14314 (1 4 1) + 0.29926 (10 7 0)
- 0.07242 (-4 5 1) + 0.00047 (-3 1 3) + 0.13909 (4 7 2) + 0.09294 (-5 4 1) + 0.00070 (-2 2 3)
- 0.17198 (-1 4 3) - 0.13339 (9 2 1) - 0.03843 (3 2 1) + 0.10150 (5 10 2) - 0.00177 (-7 5 4)
+ 0.03658 (7 4 0) + 3.35303 R = 0.999

<M1-O> = 0.40541 c - 0.02916 (-7 0 5) + 0.43407 b + 0.34608 (-7 6 5) + 0.07249 (5 4 1)
- 0.01419 β - 0.01475 (-6 2 2) + 0.02812 (-4 2 2) - 0.00705 (4 10 0) - 0.04500 (-2 3 6)
- 0.01779 (-1 1 1) + 0.00334 (-2 4 1) - 0.18254 (-3 6 4) + 0.12372 (-3 4 6) - 0.09799 (4 3 5)
+ 0.11619 (-1 6 4) - 0.00005 (-2 2 1) - 0.11425 (6 7 1) + 0.09588 ($\bar{3}$ 10 4) + 0.03097 (2 7 1)
- 2.37034 R = 0.999

m.a.n. M11 = 8.64872 a - 0.26463 (-3 1 1) + 0.00245 (4 4 0) + 0.00683 (-6 0 4) - 0.15860 (7 5 0)
+ 0.12432 (-9 3 1) + 0.64075 (1 7 1) - 0.39822 (-2 8 1) + 0.25266 (4 0 4) - 12.47638 (0 3 2)
- 0.33359 (4 0 6) - 0.79644 (9 2 1) + 0.96263 (-4 2 2) - 1.49806 (3 11 0) + 10.28124 (1 10 2)
+ 0.03467 (-1 1 4) + 0.20292 (-7 1 2) + 3.06034 (-1 2 2) + 0.27418 (3 5 0) + 0.90622 (4 10 0)
+ 10.59965 (-5 6 3) + 0.53780 (6 2 3) + 0.07083 (-3 5 2) - 6.87790 (4 9 3) + 2.23509 (-2 3 1)
+ 1.00849 (1 4 1) - 0.28228 β - 0.13599 ($\bar{12}$ 2 1) - 0.67808 (3 10 0) - 43.13688
R = 0.999

m.a.n. M1 = 0.29262 (-1 1 4) + 0.13351 (1 1 2) - 0.13868 (0 2 1) - 0.96679 (1 2 0) - 2.47508 (0 11 2)
- 0.05583 (5 1 0) + 2.47533 (1 2 1) - 16.03040 (-2 5 3) + 14.66150 (-9 0 1) + 0.05722 (4 4 0)
- 0.05437 (-6 6 2) - 5.90554 (-1 0 3) + 0.18001 (0 2 0) + 0.73542 (6 2 3) + 6.38401 (-2 9 1)
- 0.12373 (4 0 2) - 0.26382 (-2 0 2) + 5.70404 (7 6 0) - 0.59749 (2 8 1) - 3.99153 (-7 8 1)
- 0.27124 (1 3 2) + 0.09420 (3 5 2) + 1.30906 (0 7 2) + 3.73615 (1 2 2) + 0.02162 (1 5 0)
- 0.07167 (3 3 0) + 1.08392 (0 9 4) + 0.03307 ($\bar{4}$ 10 2) + 0.00374 (2 2 1) - 0.02807 (4 2 2)
+ 15.57042 R = 0.998

m.a.n. M2 = 1.94657 β - 26.42153 (3 0 5) + 2.27706 (2 2 2) + 10.44972 (-1 4 3) - 1.17440 (4 2 2)
+ 0.69662 (6 2 3) - 1.38260 (-1 0 1) - 1.31510 (4 0 6) - 38.78089 (-2 5 2) + 7.18936 (0 11 0)
+ 12.74750 (-3 8 5) + 13.96840 (3 0 3) - 0.47382 ($\bar{4}$ 10 2) - 14.28200 (2 9 3) + 0.24365 (4 10 0)
+ 11.38110 a + 0.68271 (-5 7 5) + 7.98047 (5 8 1) + 15.16658 (7 6 0) + 5.87130 (5 2 1)
- 0.17040 (1 5 2) + 0.30497 (5 7 1) - 1.33244 (-2 9 1) - 0.11380 Vol + 1.06257 (4 3 1)
+ 0.08524 (1 3 2) + 1.40302 (4 7 1) + 0.01015 (2 0 2) -255.32104 R = 0.999

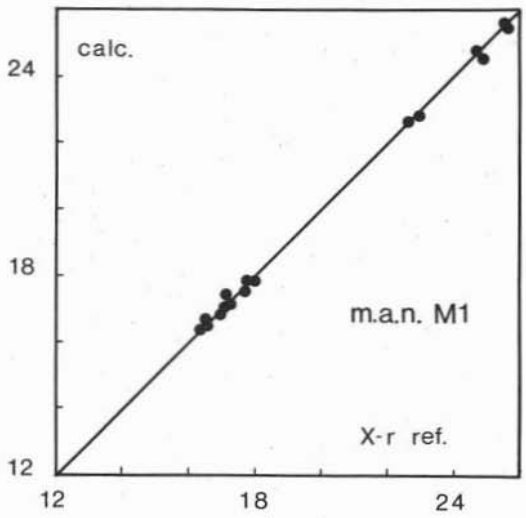
m.a.n. M21 = 0.24887 (-1 1 1) + 5.68783 (0 7 2) + 0.35249 (1 2 1) - 0.42041 (-3 5 6) + 9.75950 (-9 0 1)
+ 9.22396 (0 11 2) + 6.71398 a - 0.81289 (-6 6 2) + 0.15406 (-8 2 5) - 9.63445 (-5 4 1)
+ 24.45501 (-6 7 2) - 15.45242 (-8 5 3) + 0.86927 (6 2 3) + 0.18696 (-5 2 3) + 11.30826 (7 10 0)
- 15.93622 (3 4 4) - 0.16872 (4 2 2) - 3.40986 (3 2 1) + 4.48113 (0 1 2) + 0.35286 ($\bar{10}$ 0 6)
- 0.12335 (4 0 6) + 1.63039 (-6 3 2) - 0.09055 (3 3 1) + 0.89072 (5 2 1) - 0.52726 (4 7 4)
- 46.23021 R = 0.999

(*hkl*) means intensity of the *hkl* reflection. *K* is the multiplier to put the intensities on the absolute scale

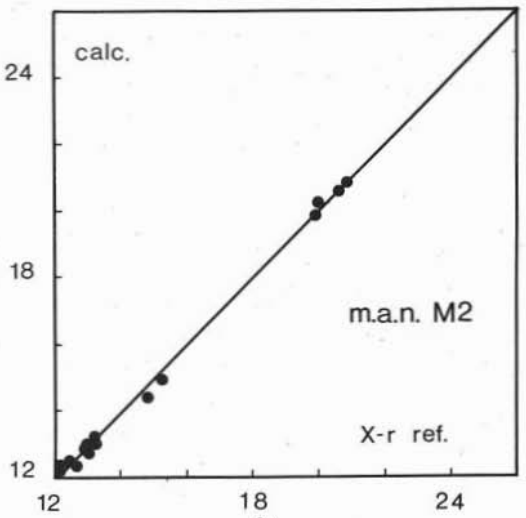
of the results. As a demonstration of the reliability of the calculated values, two examples are given in table 3, in which the comparison with the values obtained from the complete crystal-structure refinement is shown. These examples refer to the most ordered and the least ordered among the available samples.

Conclusion

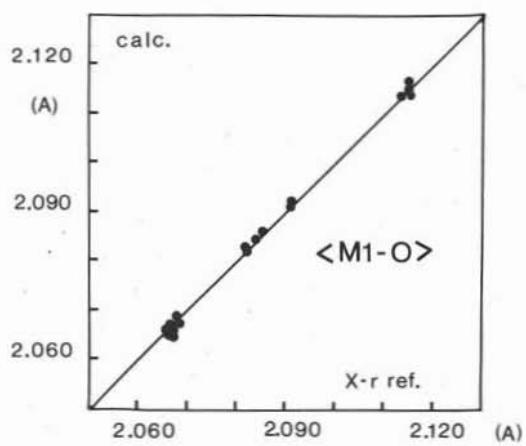
The results described in the previous section were used to write two FORTRAN programs, one for the orthopyroxenes (ORTHOPYR) and one for the clinopyroxenes (CLINOPYR). Because of their simplicity, they can be processed with any kind of available personal computer, or be



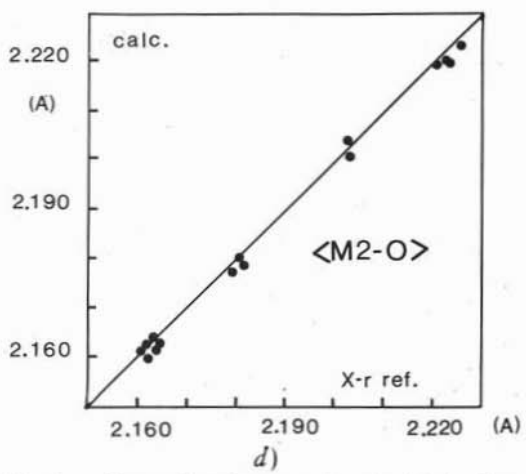
a)



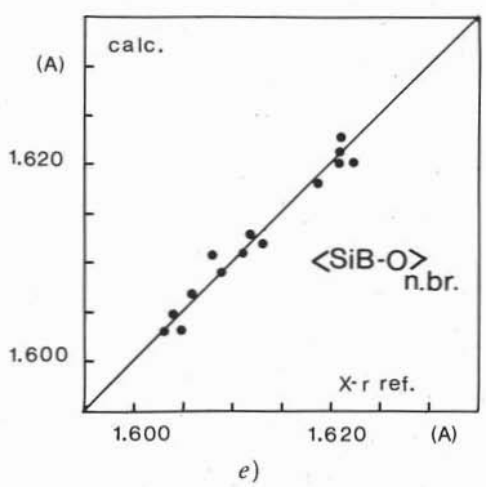
b)



c)



d)



e)

Fig. 1. — Comparison between the calculated values and those obtained from a conventional refinement of 16 orthopyroxenes: *a*) mean atomic number (number of electrons) in the M1 site; *b*) mean atomic number in the M2 site; *c*) M1-O mean distance; *d*) M2-O mean distance; *e*) SiB-$O_{n.br.}$ mean distance.

inserted in an X-ray diffractometer standard software. To enhance the accuracy of the results, a routine for the absorption correction based upon the method of NORTH, PHILLIPS and MATHEWS (1968) was also inserted in the calculation. To summarize, a standard procedure for the fast determination of the crystal-chemical variations of orthopyroxenes and omphacites consists in the accurate measurement of the unit-cell parameters and of 133 and 116 independent reflections respectively. By using the proper

TABLE 3

Comparison between the crystal-chemical parameters calculated by the CLINOPYR program and those obtained at the end of the refinements of two P2/n clinopyroxenes

	calc	obs	calc	obs
<M11 - O>	1.933	1.932	2.011	2.010
<M1 - O>	2.076	2.076	2.049	2.050
m.a.n. M11	13.45	13.51	13.83	13.78
m.a.n. M1	13.36	13.33	13.40	13.43
m.a.n. M2	13.29	13.29	14.98	14.95
m.a.n. M21	18.04	18.04	16.99	17.01

program, the intensities are experimentally corrected for absorption and put on the absolute scale; the resulting set is then used to solve the group of linear combinations by means of the coefficients reported in tables 1 and 2.

This method is completely satisfactory for the goal of this work. The whole procedure can be carried in two or three hours and the resulting crystal-chemical parameters allow either to monitor the order-disorder transformation, or to calculate the degree of order in a natural omphacite. They are also extremely useful whenever the investigation of a complex rock sample is needed, because of the possibility of quickly evidentiating the crystals which show significant crystal-chemical variations.

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