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CHARACTERIZATION OF FINE-GRAINED MIXTURES OF ROCK-FORMING MINERALS BY RIETVELD STRUCTURE REFINEMENT: OLIVINE + PYROXENE

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ABSTRACT

We have determined the modal proportions and structural details of known fine-grained mixtures of olivine and pyroxene by Rietveld structure refinement using Cu*K*α X-rays. The crystal structures of the constituent phases were refined to *R* indices of 2–3% by single-crystal methods using Mo*K*α X-rays. The structures were also refined by the Rietveld method as single phases using Cu*K*α X-rays. Comparison of the results of these experiments allows the accuracy of the procedure to be evaluated for use in typical mineral-synthesis and phase-petrology studies. Modal proportions were determined with an accuracy of 0.9% absolute and 3.0% relative, and the refined modal proportions are independent of step width in the range 0.02–0.10° 2θ step-size. Site populations and bulk compositions are accurate to within their assigned level of precision. Where the phase is minor (≤10%), the assigned precision can be too large for the results to be useful; however, for major constituents (≥10%), site populations and bulk compositions can be determined accurately and precisely. Stereochemical details are accurate, but are determined to a useful precision only where the phase is a major constituent (≥30%) of the mixture. This work shows that Rietveld structure-refinement with X rays can give accurate and precise unit-cell dimensions, site populations (structural state) and composition, modal proportion and stereochemical details for (binary) mixtures of rock-forming minerals.

Keywords: Rietveld, mixtures, modal proportions, structure refinement, olivine, pyroxene.

SOMMAIRE

Nous avons déterminé la proportion modale et les détails structuraux de mélanges connus d'olivine et de pyroxène par affinement des structures selon la méthode de Rietveld, en utilisant un rayonnement Cu*K*α. La structure des deux minéraux utilisés dans notre étude a été affinée sur cristal unique jusqu'à un résidu *R* dans l'intervalle 2–3% en utilisant un rayonnement Mo*K*α. Les structures ont aussi été affinées par la méthode de Rietveld sur échantillons monocristallins des deux minéraux en utilisant un rayonnement Cu*K*α. Une comparaison des résultats de ces expériences mène à une évaluation de la justesse du protocole à utiliser pour fins de caractérisation des produits de synthèse et d'études des équilibres de phases. Les proportions modales ont été déterminées avec une justesse de 0.9% en termes absolus, et de 3.0% en termes relatifs. Les proportions modales semblent indépendantes de l'intervalle de comptage, compris entre 0.02 et 0.10°2θ. La population des sites et la composition globale calculées sont correctes, compte tenu du niveau de précision qui leur est assigné. Dans les cas où une des deux phases est mineure (≤10%), la précision assignée peut être trop élevée pour que les résultats soient jugés utiles. Toutefois, dans le cas de proportions majeures (≥10%), la population des sites et les compositions globales peuvent être déterminées avec précision et justesse. Les détails d'ordre stéréochimique sont reproduits justement, mais ne sont évalués avec une précision utile que si une phase constitue un composant majeur (≥30%) du mélange. Ce travail montre que l'affinement des structures par diffraction X avec la méthode de Rietveld peut mener à une évaluation juste et précise des paramètres réticulaires, de l'occupation des sites structuraux, de la composition, de proportions modales et de détails stéréochimiques dans le cas de mélanges binaires de minéraux importants en pétrologie.

(Traduit par la Rédaction)

Mots-clés: Rietveld, mélanges, proportions modales, affinement de la structure, olivine, pyroxène.

INTRODUCTION

The characterization of fine-grained run-products in mineral synthesis and stability studies is a significant problem. Hawthorne (1983a), Hawthorne *et al.* (1984) and Raudsepp *et al.* (1984) advocated the use of Rietveld structure refinement for this purpose, and Raudsepp *et al.* (1987a, b, 1990a, b) have shown that, in optimum circumstances, one can derive modal proportions, structural state and composition of both phases in fine-grained binary mixtures.

Details of the Rietveld method were reviewed by Young (1980, 1993) and Post & Bish (1989). The work of Hill and coworkers (Hill & Flack 1987, Hill

& Howard 1986, 1987, Hill & Madsen 1984, 1986) and Bish and coworkers (Bish & Chipera 1988, Bish & Howard 1988, Snyder & Bish 1989, Bish & Post 1993) is of particular importance to the use of the Rietveld method for analysis of mixtures of complex minerals. In particular, Hill & Howard (1987) showed how the modal proportions of phases in a mixture can be determined from the Rietveld scale-factors. They further showed that the resulting values are both precise and accurate, provided that the relative X-ray absorption coefficients of the phases are similar. Most of the subsequent work on mixtures has involved fairly simple phases (Bish & Post 1993), and the intention of the work has been to derive modal proportions (O'Connor & Raven 1988, Snyder & Bish 1989). The principal aim of run-product characterization is usually different; the main interest focuses on degrees of order and composition of the individual phases. Of course, Rietveld structure refinement offers the possibility of determining *both* structural state (+ bulk composition) *and* modal proportions quite accurately and precisely. However, although the method has been used for complex run-products (Raudsepp *et al.* 1987a, b, Della Ventura *et al.* 1993a, b, Robert *et al.* 1993), the accuracy of the method has not been *tested* for mixtures of such complex structures; this is the object of the present work.

TABLE 1. CHEMICAL COMPOSITION AND UNIT FORMULAE OF OLIVINE AND PYROXENE

	Olivine	Pyroxene
SiO_2 wt%	39.47	53.04
Al_2O_3	0.02	1.84
TiO_2	0.01	0.10
Cr_2O_3	0.02	0.02
FeO	11.36	1.28
MnO	0.19	0.04
NiO	0.36	0.03
MgO	47.51	17.84
CaO	0.20	25.58
Na_2O	–	0.05
Total	99.14	99.82
Si	0.987	1.932
Al	0.001	0.079
Ti	–	0.003
Cr	–	0.001
Fe	0.237	0.039
Mn	0.004	0.001
Ni	0.007	0.001
Mg	1.770	0.969
Ca	0.005	0.999
Na	–	0.004
O	4	6

EXPERIMENTAL

Materials

An olivine separate was produced by magnetic separation and hand picking from a dunite (volcanic bomb) from Hawaii. The pyroxene sample is from Laurel, Argenteuil Co., Quebec. It is a diopside and occurs intimately mixed with calcite; euhedral pyroxene crystals were easily detached, crushed and washed in dilute HCl to remove calcite impurities. Binary mixtures of olivine and pyroxene were prepared at 10 wt% intervals.

Electron-microprobe analysis

Crystals of olivine and pyroxene were analyzed by electron microprobe using a CAMECA SX–50

TABLE 2. DETAILS OF STRUCTURE REFINEMENT WITH POWDER X-RAY DATA

		Olivine (Ol)	Pyroxene (Px)	P1	P2	P3	P4	P5	P6	P7	P8	P9
Range (°2θ)		16–136	18–138	16–136	16–136	19–139	19–139	19–139	16–136	16–136	19–139	19–139
*SF	Ol	13.7(2)		1.2(1)	2.4(2)	3.7(1)	7.6(2)	10.6(3)	11.5(3)	18.1(4)	22.0(4)	19.3(3)
	Px		6.2(1)	5.21(7)	4.67(7)	3.60(6)	5.36(6)	4.88(9)	3.77(7)	3.7(1)	2.71(7)	1.21(7)
+N–p		1111	2367	2343	2343	2343	2343	2343	2343	2343	2344	2344
R_p(%)		8.7	9.3	9.4	9.4	9.7	7.1	7.5	7.6	8.0	6.7	7.2
R_{wp}		11.9	12.9	12.5	12.4	13.0	9.6	10.3	10.1	13.8	8.8	9.8
R_B	Ol	3.7		4.1	3.6	3.8	2.5	2.8	2.9	3.0	3.1	2.6
	Px		3.6	4.5	4.9	4.4	2.5	3.7	3.5	6.3	3.0	2.4
**D–W		1.26	1.19	0.86	1.08	1.25	1.38	1.32	1.20	2.04	1.04	1.21

[*] SF = scale factor (x 10^4)

[+] N–p = number of observations – number of variables; R_p = R index for pattern, R_{wp} = weighted R index for pattern; R_B = R index for structure (i.e. for the Bragg peaks).

[**] D–W = Durbin-Watson statistic

operating in the wavelength-dispersion mode. Backscattered electron images showed no discernable zoning in either mineral. Experimental details are as described by Hawthorne *et al.* (1993). Mean compositions and unit formulae are given in Table 1.

Collection of X-ray data

A Philips 1710 powder diffractometer was used in the collection of the powder-diffraction intensity data; details of the experimental procedure are given by Raudsepp *et al.* (1990a). The step-width increment was 0.05° 2θ. For the 1:1 mixture, we also collected data with a step width of 0.01° 2θ to examine the effect of step-width variation on the results of the refinement. The count time at each step was between 2–3 s, with a maximum intensity of 2000–3000 counts. Other experimental details are given in Table 2.

TABLE 3. SINGLE-CRYSTAL X-RAY DIFFRACTION DATA COLLECTION AND REFINEMENT INFORMATION FOR OLIVINE AND PYROXENE

	Olivine	Pyroxene
a (Å)	4.764(1)	9.743(2)
b	10.226(3)	8.916(2)
c	6.004(2)	5.256(1)
β (°)		105.88(1)
V (Å^3)	292.5(1)	439.1(1)
Space group	*Pbnm*	*C2/c*
Z	4	4
Crystal size (mm)	0.28 x 0.31 x 0.32	0.32 x 0.26 x 0.22
Radiation	Mo*Kα*	Mo*Kα*
Monochromator	Graphite	Graphite
R(azimuthal) %	1.74	1.34
Total no. |F|	462	649
No. of |F|$_{obs}$	458	648
R_{obs} %	2.4	3.2
wR_{obs} %	2.8	3.6

$R = \Sigma(|F|-|F|)/\Sigma|F|$

$wR = [\Sigma w(|F|-|F|)^2/\Sigma wF^2]^{0.5}\ w=1$

Rietveld structure refinement

Structures were refined using the program LHPM1 [originally written as DBW3.2 by Wiles & Young (1981) and modified by Hill & Howard (1986)]. A pseudo-Voigt peak-shape was used (with variable-percentage Lorentzian character), the FWHM (full peak-width at half-maximum height) was varied as a function of 2θ using the expression of Caglioti *et al.* (1958), and the peak asymmetry was corrected using the function of Rietveld (1969). Structural variables included atomic coordinates, *M*-site occupancies, and an overall isotropic-displacement factor; nonstructural variables were scale factor(s) and parameters for background correction, peak shape and asymmetry, and a preferred-orientation correction. Single-phase refinements of olivine and pyroxene were done as a measure of the optimal agreement to be expected between the Rietveld and single-crystal refinements. Individual isotropic-displacement parameters were fixed at "reasonable" values (*i.e.*, the relative sizes of the parameters were taken from single-crystal work on analogous crystals) and an overall displacement-parameter was refined to scale the individual values. Those site occupancies taken as variable were refined without constraints of any sort. Refinement was terminated when the maximum parameter-shift or error was less than 0.01.

For refinement of the mixtures, there were 58 variable parameters. Otherwise, refinement was similar to the single-phase refinements except for the presence of two structures and two scale factors. Again, refinement was terminated when the maximum shift or error was less than 0.01. Details of structure refinements are given in Table 2.

Two additional phases of refinement were done to investigate the effect of two specific factors on the refinement results. The 1:1 mixture was refined

TABLE 4. REFINED CELL-DIMENSIONS FOR OLIVINE AND PYROXENE

Sample no.	Olivine wt%	Olivine				Pyroxene				
		a (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)	*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)	*V* (Å^3)
SC		4.7642(14)	10.2258(28)	6.0045(18)	292.53	9.7429(19)	8.9161(15)	5.2557(10)	105.880(14)	439.14
SPh	100	4.7649(3)	10.2376(6)	5.9986(4)	292.61	9.7476(5)	8.9174(4)	5.2573(3)	105.900(4)	439.49
P1	9.9	4.7673(21)	10.249(4)	5.9996(20)	293.14	9.7501(8)	8.9207(7)	5.2593(4)	105.897(5)	439.94
P2	19.9	4.7659(12)	10.2414(20)	5.9983(12)	292.75	9.7497(9)	8.9189(7)	5.2576(4)	105.903(5)	439.68
P3	30.6	4.7654(4)	10.2396(13)	5.9984(8)	292.66	9.7489(9)	8.9181(8)	5.2574(5)	105.888(6)	439.62
P4	39.7	4.7652(4)	10.2388(8)	5.9992(5)	292.68	9.7489(7)	8.9184(6)	5.2577(3)	105.896(5)	439.65
P5	49.9	4.7651(4)	10.2385(8)	5.9983(5)	292.61	9.7485(8)	8.9179(7)	5.2566(4)	105.894(6)	439.52
P6	59.9	4.7644(3)	10.2370(6)	5.9975(4)	292.52	9.7464(9)	8.9163(8)	5.2562(5)	105.897(7)	439.30
P7	70.0	4.7649(4)	10.2370(7)	5.9980(4)	292.58	9.7493(14)	8.9142(12)	5.2564(8)	105.893(11)	439.36
P8	79.9	4.7659(3)	10.2396(6)	5.9993(2)	292.77	9.7498(16)	8.9160(15)	5.2586(9)	105.872(13)	439.70
P9	89.6	4.7660(3)	10.2379(5)	5.9992(3)	292.72	9.747(4)	8.914(3)	5.2590(24)	105.90(3)	439.46

TABLE 5. ATOMIC POSITIONS FOR OLIVINE AND PYROXENE

		SC	SPh	P1	P2	P3	P4	P5	P6	P7	P8	P9
							Olivine					
M(1)	x	0	0	0	0	0	0	0	0	0	0	0
	y	0	0	0	0	0	0	0	0	0	0	0
	z	0	0	0	0	0	0	0	0	0	0	0
	B(Å²)	0.40(1)										
M(2)	x	0.98978(18)	0.9924(12)	0.998(10)	0.990(5)	0.990(10)	0.990(2)	0.988(2)	0.988(1)	0.990(1)	0.990(1)	0.990(1)
	y	0.27774(8)	0.2769(4)	0.273(3)	0.277(2)	0.278(3)	0.278(1)	0.277(1)	0.277(1)	0.277(1)	0.2774(3)	0.2778(4)
	z	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4
	B(Å²)	0.41(2)										
T	x	0.42657(16)	0.4288(6)	0.428(7)	0.420(4)	0.427(6)	0.428(1)	0.427(1)	0.427(1)	0.427(1)	0.428(1)	0.428(1)
	y	0.09441(7)	0.0949(5)	0.107(3)	0.096(2)	0.095(3)	0.095(1)	0.095(1)	0.096(1)	0.095(1)	0.095(4)	0.095(4)
	z	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4
	B(Å²)	0.39(2)										
O(1)	x	0.7666(4)	0.7655(18)	0.782(18)	0.766(8)	0.769(4)	0.768(3)	0.769(3)	0.763(2)	0.765(2)	0.767(2)	0.768(2)
	y	0.0917(19)	0.0896(12)	0.081(8)	0.093(4)	0.095(2)	0.092(2)	0.090(2)	0.091(1)	0.091(1)	0.090(1)	0.089(1)
	z	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4
	B(Å²)	0.50(4)										
O(2)	x	0.2199(4)	0.2197(19)	0.195(16)	0.223(8)	0.207(4)	0.217(3)	0.220(3)	0.216(2)	0.218(2)	0.216(2)	0.217(2)
	y	0.44786(18)	0.4477(12)	0.439(8)	0.443(3)	0.445(3)	0.443(2)	0.445(2)	0.446(1)	0.446(1)	0.446(1)	0.446(1)
	z	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4
	B(Å²)	0.48(4)										
O(3)	x	0.27883(28)	0.2784(14)	0.202(12)	0.264(6)	0.276(3)	0.273(3)	0.272(2)	0.275(2)	0.278(2)	0.279(1)	0.278(1)
	y	0.16332(12)	0.1639(8)	0.163(5)	0.167(3)	0.164(2)	0.163(1)	0.163(1)	0.162(1)	0.163(1)	0.162(1)	0.161(1)
	z	0.03370(22)	0.0318(13)	0.017(9)	0.023(5)	0.030(3)	0.032(2)	0.031(2)	0.031(1)	0.032(1)	0.030(1)	0.032(1)
	B(Å²)	0.52(3)										
							Pyroxene					
M(1)	x	0	0	0	0	0	0	0	0	0	0	0
	y	0.90818(14)	0.908(1)	0.906(1)	0.908(1)	0.908(1)	0.907(1)	0.907(1)	0.907(1)	0.907(2)	0.905(2)	0.898(5)
	z	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4
	B(Å²)	0.38(3)										
M(2)	x	0	0	0	0	0	0	0	0	0	0	0
	y	0.30152(9)	0.301(1)	0.302(1)	0.301(1)	0.302(1)	0.302(1)	0.302(1)	0.300(1)	0.300(1)	0.302(2)	0.299(3)
	z	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4
	B(Å²)	0.67(2)										
T	x	0.28645(7)	0.288(5)	0.287(1)	0.288(1)	0.287(1)	0.287(1)	0.288(1)	0.287(1)	0.288(1)	0.287(1)	0.293(1)
	y	0.09328(8)	0.094(1)	0.094(1)	0.094(1)	0.093(1)	0.093(1)	0.094(1)	0.092(1)	0.091(1)	0.092(2)	0.090(3)
	z	0.22934(14)	0.230(1)	0.232(1)	0.233(1)	0.231(1)	0.231(1)	0.231(1)	0.234(1)	0.229(2)	0.230(2)	0.234(4)
	B(Å²)	0.42(1)										
O(1)	x	0.11533(22)	0.115(1)	0.115(1)	0.113(1)	0.114(1)	0.116(1)	0.115(1)	0.113(1)	0.113(2)	0.111(2)	0.118(5)
	y	0.08722(22)	0.088(1)	0.091(1)	0.089(1)	0.089(1)	0.090(1)	0.089(2)	0.090(2)	0.089(3)	0.089(3)	0.080(6)
	z	0.14135(36)	0.143(2)	0.138(2)	0.140(2)	0.135(2)	0.140(2)	0.140(2)	0.137(3)	0.136(4)	0.137(5)	0.145(11)
	B(Å²)	0.56(4)										
O(2)	x	0.36136(21)	0.363(1)	0.363(1)	0.365(1)	0.365(1)	0.364(1)	0.364(1)	0.366(1)	0.365(3)	0.368(3)	0.366(6)
	y	0.25015(23)	0.252(3)	0.250(1)	0.250(1)	0.250(1)	0.250(1)	0.251(1)	0.253(2)	0.251(3)	0.250(3)	0.250(6)
	z	0.31912(38)	0.320(2)	0.322(2)	0.321(2)	0.318(2)	0.319(2)	0.321(2)	0.325(3)	0.327(4)	0.327(4)	0.320(9)
	B(Å²)	0.70(4)										
O(3)	x	0.35085(20)	0.353(1)	0.352(1)	0.349(1)	0.350(1)	0.352(1)	0.352(2)	0.353(2)	0.355(3)	0.358(3)	0.368(5)
	y	0.01806(22)	0.019(1)	0.018(1)	0.020(1)	0.020(1)	0.021(1)	0.019(1)	0.023(2)	0.025(3)	0.021(2)	0.028(6)
	z	0.99519(37)	0.999(2)	0.004(2)	0.003(2)	0.998(3)	0.000(2)	0.007(3)	0.005(3)	0.010(5)	0.010(5)	0.023(12)
	B(Å²)	0.62(4)										

TABLE 6. REFINED M-SITE POPULATIONS FOR OLIVINE AND PYROXENE

		SC	SPh	P1	P2	P3	P4	P5	P6	P7	P8	P9
							Olivine					
M1	Mg	0.904(3)	0.924(7)	0.82(6)	0.854(28)	0.872(14)	0.918(10)	0.902(11)	0.906(7)	0.902(8)	0.910(6)	0.902(6)
	Fe	0.096(3)	0.076(7)	0.18(6)	0.146(28)	0.128(14)	0.082(10)	0.098(11)	0.094(7)	0.098(8)	0.090(6)	0.098(6)
M2	Mg	0.912(3)	0.898(6)	0.902(41)	0.900(21)	0.900(13)	0.898(10)	0.902(10)	0.894(7)	0.898(7)	0.900(6)	0.900(6)
	Fe	0.088(3)	0.102(6)	0.098(41)	0.100(21)	0.100(13)	0.102(10)	0.098(10)	0.106(7)	0.102(7)	0.100(6)	0.100(6)
							Pyroxene					
M1	Mg	0.992(4)	0.992(7)	0.984(8)	0.970(8)	0.982(10)	0.948(8)	0.976(11)	0.990(11)	0.992(17)	0.998(20)	0.962(41)
	Fe	0.008(4)	0.008(7)	0.016(8)	0.030(8)	0.018(10)	0.052(8)	0.024(11)	0.010(11)	0.008(17)	0.002(20)	0.038(41)
M2	Mg	0.000(38)	0.038(7)	0.016(10)	0.024(10)	0.020(13)	0.040(10)	0.008(13)	0.026(14)	0.022(21)	−0.016(26)	0.04(6)
	Fe	0.029(38)	−0.008(7)	0.008(10)	0.008(10)	0.004(13)	−0.012(10)	0.020(13)	0.004(14)	0.008(21)	0.044(26)	0.00(6)

at different step-intervals from 0.02–0.10° 2θ in order to test whether the step interval has a significant effect on the accuracy of the results (we know it has a significant effect on the *precision via* serial correlation). In addition, we also refined the mixtures with all structural parameters for both olivine and pyroxene fixed at their single-crystal values in order to see if there was an interaction between the scale factor and the structural parameters, such that compensating errors in both could give a good fit to the pattern but inaccurate results.

TABLE 7. SELECTED ATOMIC DISTANCES (Å) IN OLIVINE AND PYROXENE

Sample No.	SC	SPh	P1	P2	P3	P4	P5	P6	P7	P8	P9
Olivine wt%			9.9	19.9	30.6	39.9	49.9	59.9	70.0	79.9	89.6
						Olivine					
T-O1	1.620(2)	1.603(6)	1.71(9)	1.65(4)	1.63(3)	1.623(15)	1.626(15)	1.603(11)	1.608(11)	1.620(8)	1.622(7)
T-O2	1.653(2)	1.663(12)	1.82(3)	1.71(5)	1.66(4)	1.698(20)	1.692(20)	1.680(16)	1.677(16)	1.673(11)	1.673(12)
T-O3	1.637(2)	1.647(17)	1.86(4)	1.72(4)	1.659(27)	1.654(12)	1.660(12)	1.645(10)	1.647(10)	1.647(8)	1.638(7)
mean	1.637(1)	1.638(7)	1.80(3)	1.69(2)	1.65(2)	1.658(9)	1.659(9)	1.643(7)	1.644(7)	1.647(5)	1.644(5)
M1-O1	2.090(2)	2.084(14)	2.00(6)	2.10(3)	2.102(16)	2.086(10)	2.077(10)	2.095(8)	2.092(9)	2.081(6)	2.075(6)
M1-O2	2.078(2)	2.079(13)	2.18(7)	2.082(28)	2.124(16)	2.099(10)	2.087(10)	2.094(7)	2.089(9)	2.093(6)	2.089(6)
M1-O3	2.143(2)	2.147(12)	1.93(5)	2.126(18)	2.141(16)	2.126(12)	2.119(10)	2.127(8)	2.138(9)	2.134(6)	2.126(6)
mean	2.104(1)	2.103(8)	2.04(3)	2.103(15)	2.092(9)	2.104(6)	2.094(6)	2.105(4)	2.104(5)	2.103(3)	2.097(3)
M2-O1	2.179(2)	2.201(16)	2.22(8)	2.16(4)	2.14(4)	2.181(17)	2.179(16)	2.187(13)	2.183(14)	2.192(9)	2.200(9)
M2-O2	2.056(2)	2.058(14)	1.94(9)	2.03(4)	2.00(4)	2.007(17)	2.044(18)	2.039(14)	2.039(14)	2.037(10)	2.039(10)
M2-O3a	2.225(2)	2.217(13)	2.23(5)	2.20(3)	2.22(3)	2.217(10)	2.222(10)	2.231(8)	2.228(9)	2.244(6)	2.237(6)
M2-O3b	2.068(2)	2.067(12)	2.05(5)	2.04(4)	2.06(3)	2.073(12)	2.067(12)	2.062(10)	2.061(10)	2.055(8)	2.069(7)
mean	2.137(1)	2.138(7)	2.12(3)	2.11(2)	2.12(2)	2.128(7)	2.134(7)	2.135(6)	2.133(6)	2.138(4)	2.142(4)
						Pyroxene					
T-O1	1.604(2)	1.617(8)	1.617(9)	1.639(9)	1.623(9)	1.610(8)	1.625(11)	1.632(11)	1.635(18)	1.654(20)	1.64(4)
T-O2	1.588(2)	1.601(10)	1.586(9)	1.589(10)	1.600(11)	1.595(8)	1.595(12)	1.636(13)	1.629(20)	1.626(23)	1.60(5)
T-O3a	1.668(2)	1.659(11)	1.649(10)	1.630(12)	1.648(12)	1.644(11)	1.622(14)	1.626(16)	1.589(23)	1.622(26)	1.59(6)
T-O3b	1.689(2)	1.714(11)	1.715(14)	1.715(12)	1.699(14)	1.743(11)	1.735(15)	1.732(16)	1.776(24)	1.765(26)	1.83(6)
mean	1.637(1)	1.648(5)	1.642(5)	1.643(5)	1.642(6)	1.648(5)	1.644(6)	1.656(7)	1.657(11)	1.667(12)	1.66(26)
M1-O1	2.057(2)	2.064(11)	2.043(9)	2.045(9)	2.027(11)	2.050(8)	2.050(12)	2.033(13)	2.027(20)	2.029(22)	2.09(5)
M1-O1a	2.119(2)	2.118(8)	2.160(12)	2.123(12)	2.139(14)	2.151(12)	2.135(15)	2.141(17)	2.142(26)	2.14(3)	2.14(6)
M1-O2a	2.052(2)	2.031(8)	2.035(10)	2.032(12)	2.023(15)	2.030(12)	2.030(15)	2.009(17)	2.024(26)	2.010(24)	1.96(7)
mean	2.076(1)	2.071(5)	2.079(6)	2.067(6)	2.063(8)	2.077(6)	2.072(8)	2.061(9)	2.070(14)	2.060(15)	2.06(3)
M2-O1	2.364(2)	2.354(10)	2.345(10)	2.335(10)	2.361(12)	2.356(10)	2.360(14)	2.328(16)	2.337(24)	2.337(29)	2.41(6)
M2-O2	2.343(2)	2.338(8)	2.327(9)	2.321(9)	2.335(11)	2.338(8)	2.327(12)	2.306(11)	2.297(19)	2.290(21)	2.32(4)
M2-O3a	2.563(2)	2.557(10)	2.541(10)	2.573(10)	2.570(12)	2.566(9)	2.535(14)	2.580(14)	2.582(14)	2.525(22)	2.53(5)
M2-O3b	2.718(2)	2.712(13)	2.738(12)	2.750(13)	2.722(15)	2.710(12)	2.737(15)	2.723(17)	2.713(26)	2.702(29)	2.66(7)
mean	2.497(1)	2.490(5)	2.488(5)	2.500(5)	2.497(6)	2.492(5)	2.490(7)	2.484(7)	2.482(11)	2.463(13)	2.48(3)

Collection and refinement of single-crystal X-ray intensity data

Single crystals of olivine and pyroxene were ground to spheres and mounted on a Nicolet *R*3*m* automated four-circle diffractometer. Cell dimensions (Table 3) were refined from the setting angles of 25 automatically aligned intense reflections. Intensity data were collected according to the procedure of Hawthorne & Groat (1985). Absorption corrections were done with the psi-scan method, modeling the crystal shape as a triaxial ellipsoid of variable shape and orientation. Intensities were corrected for background, absorption, Lorentz and polarization effects, and reduced to structure factors. Details concerning these procedures are given in Table 3.

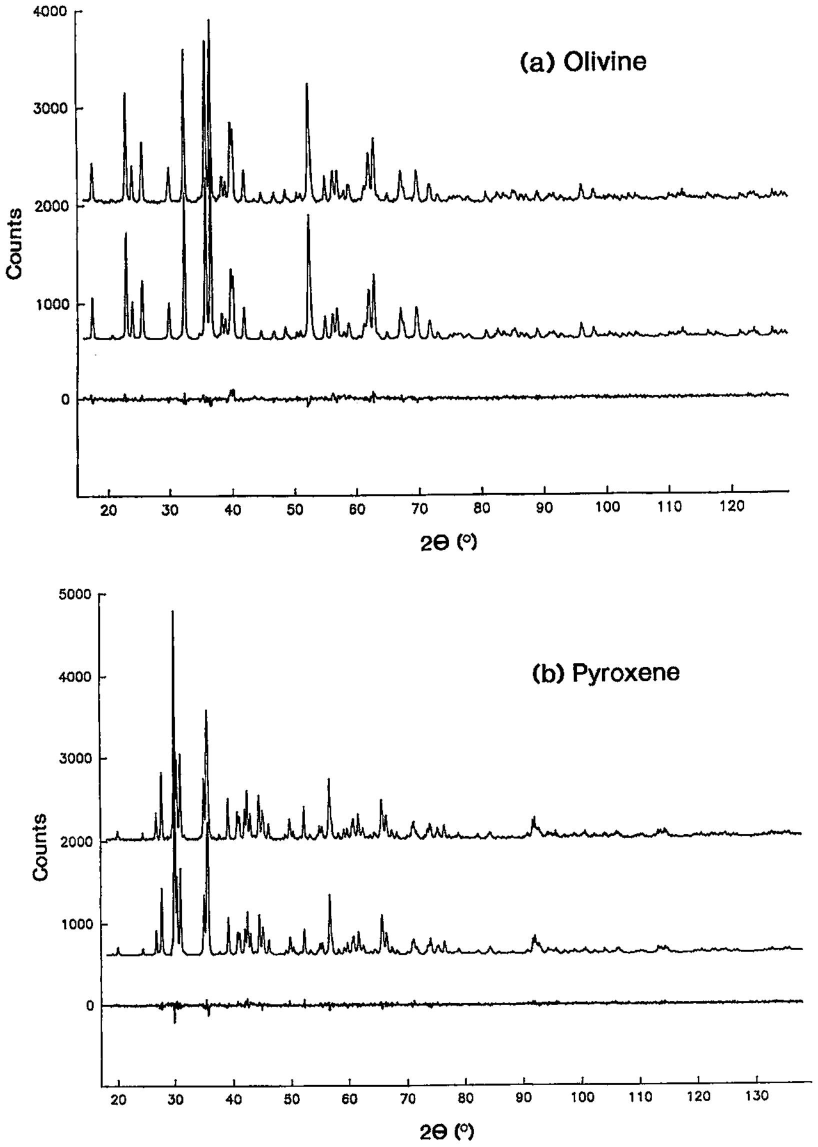

FIG. 1. Observed (upper), calculated (middle) and difference (lower) X-ray powder-diffraction patterns from each single-phase refinement: (a) olivine; (b) pyroxene; the observed and calculated patterns are displaced vertically (by adding 2000 and 600 counts to every data point in each respective pattern) to avoid pattern overlap.

Crystal structures were refined using the SHELXTL–PC system of programs; R indices are of the form given in Table 3. Full-matrix least-squares refinement converged to R indices of 2–3% for an anisotropic displacement model in which the site occupancies were refined unconstrained.

RESULTS

Cell dimensions are given in Table 4, positional parameters in Table 5, site populations in Table 6, and selected interatomic distances in Table 7. Structure-factor tables and powder-diffraction step-scan intensities may be obtained from The Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

Single-crystal refinements

The results of the single-crystal structure refinements agree closely with the results of previous refinements of olivine and calcic pyroxene structures. The refined site-populations (Table 6) agree almost exactly with the bulk compositions of the crystals as determined by EMPA (electron-microprobe analysis) and SREF (single-crystal site-scattering refinement): olivine: EMPA: $Mg_{1.77}Fe^{*}_{0.25}SiO_4$; SREF: $Mg_{1.82}Fe_{0.18}SiO_4$; pyroxene: EMPA: $Ca_{1.00}Mg_{0.97}Fe^{*}_{0.04}Si_2O_6$; SREF: $Ca_{0.99}Mg_{0.99}Fe_{0.03}Si_2O_6$ ($Fe^{*} = Fe + Ni + Mn$).

Single-phase Rietveld refinements

Figure 1 shows the observed, calculated and difference X-ray powder-diffraction patterns from each single-phase refinement. As shown in Table 6, the site populations from the single-phase Rietveld refinements are statistically identical with the values from the single-crystal refinement. The single-crystal and Rietveld positional parameters can be compared using half-normal probability analysis (Abrahams & Keve 1971). If the data sets contain random normal distributions of errors, a half-normal probability plot should give a linear plot of unit slope with zero intercept, provided that the standard deviations are correct. We know that serial correlation in the powder-diffraction data leads to incorrect standard deviations, a measure of which is the Durbin–Watson statistic (Hill & Flack 1987). This problem was corrected using the procedure of Bérar & Lelann (1991); the assigned standard deviations given in the Tables are the corrected values.

Multiphase Rietveld refinements

Figure 2 shows a typical observed, calculated and difference X-ray powder-diffraction pattern for a multiphase refinement. The modal percentages of olivine and pyroxene were calculated from the following equation (Hill & Howard 1987):

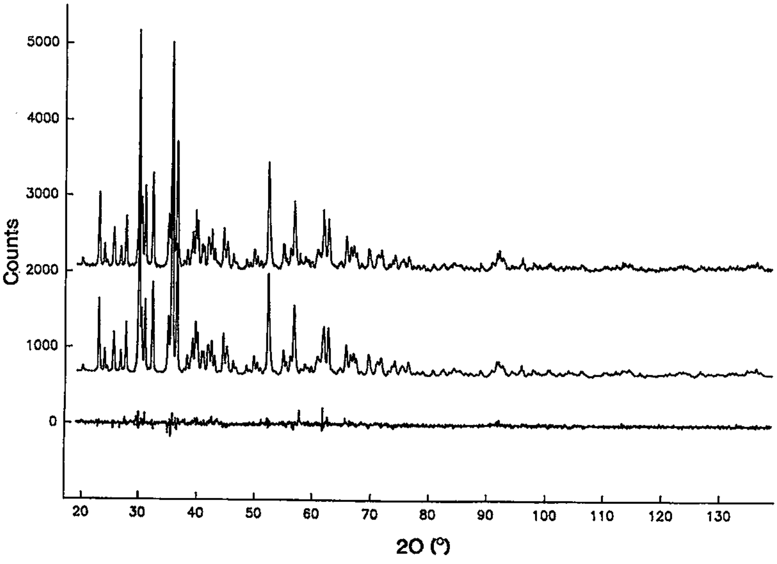

FIG. 2. Typical observed (upper, plus 2000 counts), calculated (middle, plus 600 counts) and difference (lower) X-ray powder-diffraction patterns for a multiphase refinement of the 50:50 olivine:pyroxene mixture.

TABLE 8. MODAL PROPORTION OF OLIVINE (wt%) IN THE OLIVINE-PYROXENE MIXTURES BY RIETVELD REFINEMENT

		P1	P2	P3	P4	P5	P6	P7	P8	P9
	*(1)	9.3(3)	19.7(3)	33.8(4)	39.8(4)	50.5(5)	59.4(6)	69.6(9)	80.0(14)	90.3(15)
Refined	(2)	8.8(3)	19.2(4)	33.8(5)	39.5(5)	49.8(7)	59.3(8)	69.2(9)	79.5(11)	88.3(13)
	(3)	9.1(6)	18.7(7)	31.7(10)	39.1(10)	49.7(15)	58.0(16)	68.8(25)	78.7(22)	89.9(28)
Actual		9.9	19.9	30.6	39.9	49.9	59.9	70.0	79.9	89.6

*(1) Background and scale factor only refined; structural parameters fixed at single-crystal values, instrument parameters fixed at single-phase refinement values.

(2) Background, scale factor and instrument parameters refined; structural parameters fixed at single-crystal values.

(3) Full multi-phase refinement with all possible variable parameters refined.

$$W_p = \frac{S_p(ZMV)_p}{S_p(ZMV)_p + S_q(ZMV)_q} \qquad (1)$$

in which S is the refined scale-factor, Z is the number of formula units per unit cell (Z = 4 for both olivine and $C2/m$ pyroxene), M is the mass of the formula unit, and V is the unit-cell volume; p and q represent the phases in the mixture. The values for M and V were those determined from the multiphase refinements, thus simulating the normal experimental situation in which M and V are determined from the refinement that also determines the values of S; Table 8 shows the calculated modal proportions.

DISCUSSION

Modal proportions

A graphical comparison of the refined and known modal proportion of olivine is given in Figure 3; the refined modal proportions agree with the known values within the estimated standard deviations. The mean value of the absolute accuracy across all compositions is 0.9%; the relative value is 2.3% (omitting the sample lowest in olivine) and 3.0% for all mixtures. Thus the refined modal proportions are accurate to within their assigned level of precision.

We also derived the modal proportions by refinement with fixed structural and instrumental parameters (derived from the single-phase Rietveld refinements), and with fixed structural and variable instrumental parameters. The modal proportions calculated were very similar to the full-refinement results, with mean absolute deviations of 0.7 and 0.9%, respectively, compared to the full-refinement value of 0.9% absolute.

Effect of step width on modal values

Table 9 and Figure 3 show the variation in refined modal proportion of olivine for the 1:1 mixture as a function of step width from 0.02 to 0.10° 2θ. The refined values (by all three different methods) do not vary significantly with step width; accurate values are obtained up to a step width of 0.1° 2θ. Of course, the normally assigned standard deviations increase with increasing step-width (because of decreasing serial correlation); however, the variation disappears with correction *via* the method of Bérar & Lelann (1991).

Cell dimensions

The cell dimensions from the single-crystal refinements and the single-phase and multiphase Rietveld refinements are shown in Table 4. The values obtained

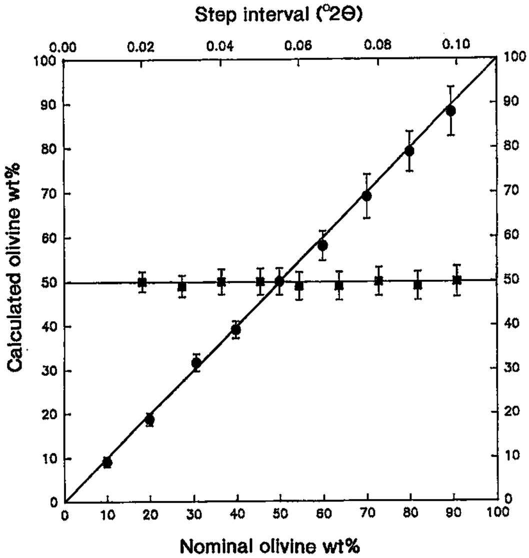

FIG. 3. Modal proportion of olivine derived from Rietveld structure refinement compared with the known modal proportions (full circles), and values for the 1:1 mixture (full squares) as a function of step width; the diagonal line is drawn through zero with a slope of 1; the horizontal line is drawn through 50% olivine with a slope of 0.

TABLE 9. MODAL PROPORTION OF OLIVINE (wt%) IN THE 1:1 OLIVINE-PYROXENE MIXTURE FOR DIFFERENT STEP-WIDTHS

Step width (°)		0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10
	*(1)	49.4(4)	50.5(5)	50.2(6)	50.0(5)	49.9(5)	49.9(6)	50.0(6)	49.7(6)	50.6(6)
Refined	(2)	49.6(6)	50.7(7)	50.0(7)	49.8(7)	49.9(7)	49.8(7)	49.6(7)	49.4(7)	49.9(8)
	(3)	49.8(11)	49.4(12)	49.6(14)	49.7(15)	49.4(15)	49.4(16)	49.9(16)	49.3(16)	50.1(17)
Actual		49.9	49.9	49.9	49.9	49.9	49.9	49.9	49.9	49.9

*(1) Background and scale factor only refined; structural parameters fixed at single-crystal values, instrument parameters fixed at single-phase refinement values. The standard deviations were calculated solely from the assigned standard deviations for the scale factors; no allowance was made for possible errors in composition and cell volume.

(2) Background, scale factor and instrument parameters refined; structural parameters fixed at single-crystal values.

(3) Full multi-phase refinement with all possible variable parameters refined.

from the single-phase and multiphase Rietveld refinements are fairly consistent. Where the phase is minor (*i.e.*, 10% of the mixture), the actual values can differ more from the mean value than the rest of the values (*e.g.*, *b* for olivine in sample P1, *a* for pyroxene in sample P9); however, the assigned standard deviations are also significantly larger in these cases, and these larger discrepancies are actually not significant (*i.e.*, $<2.5\sigma$). There are significant differences between the cell dimensions derived for powder and single crystals. In particular, *b* for olivine is ~ 0.012 Å longer for the Rietveld determinations, a difference of approximately four pooled standard deviations. We have observed here and in previous work that cell dimensions and bond lengths of single crystals do tend to be slightly shorter than corresponding powder-diffraction measurements.

Cell dimensions for the 1:1 mixture (sample P5) were measured at a series of step widths from 0.02 to 0.10° 2θ. The values obtained were found to be independent of step width in this interval. Of course, as the step width approaches the peak width, information is rapidly lost, and the refinement degrades. However, when the step width is significantly narrower than the peak width, the refinement results are not sensitive to step width. This information is useful in optimizing data-collection efficiency.

Site populations and bulk compositions

Site populations are listed in Table 6. For the olivine, there are no significant differences between the values from the single-crystal and the single-phase Rietveld refinements. Where olivine is a minor phase (*i.e.*, 10% as in P1), there can be large differences between the actual value (as determined by all of the other refinements) and the refined value; the most notable case is for Mg at *M*1 in mixture P1 (Table 6), in which the relevant values are ~0.90(6) and 0.82(8). However, although the difference is large, so are the assigned standard deviations, and the value is accurate although very imprecise. With similar amounts of both phases, both accuracy and precision are good. The situation is similar for pyroxene, although the deviations at low amounts of the phase are actually less than for olivine. Because there are three scattering species (Ca,Fe,Mg) potentially occupying the *M*2 site in pyroxene, the site populations cannot be determined just from structure refinement (Hawthorne 1983b). However, as the Ca content (of *M*2) is known from the electron-microprobe analysis, we can fix this value and refine the Mg and Fe contents of *M*2. The agreement across the complete set of data is good (Table 6). Thus for both olivine and pyroxene, we can accurately determine the site occupancies, but we must pay attention to the variation in the magnitude of the standard deviations, which vary significantly with the modal proportion of each phase.

Atomic positions and interatomic distances

The half-normal probability analysis of the Rietveld and single-crystal results for the atomic positions in the olivine (Fig. 4a) shows a nearly linear distribution with zero intercept and a slope of 1.3 (as compared to the ideal value of 1.0). The linearity shows that there is no systematic difference between the Rietveld and the single-crystal refinements, but the slope of about 1.3 indicates that the standard deviations in the Rietveld refinement are still slightly underestimated (by a factor of 1.3) even after correction for serial correlation. For the pyroxene (Fig. 2b), the distribution is slightly nonlinear with a small non-zero intercept, indicative of some error. However, omission of the two largest deviations does result in a linear distribution with zero intercept, and a slope similar to that for the olivine, indicating that two of the refined parameters (*x* coordinates at the *T* and the O3 sites) are in error.

Different sets of refinement of the same phase can more easily be compared using the interatomic distances. For the olivine, there is very good agreement between the important bond-lengths determined by single-crystal refinement and by single-phase Rietveld refinement (Table 7). The maximum differences are 0.022(16) Å for *M*2–O1 and 0.017(6) Å for *T*–O1;

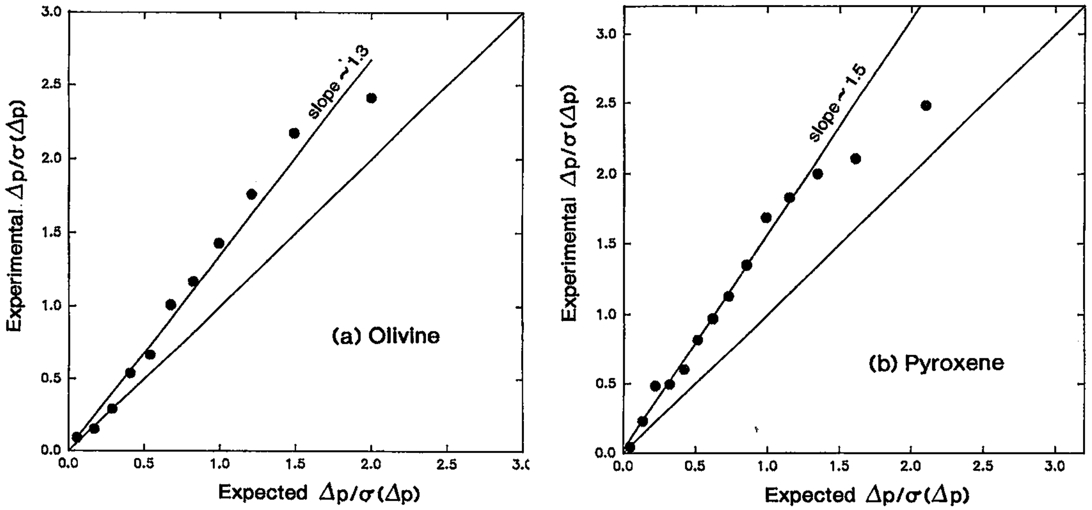

FIG. 4. Half-normal probability plots for the atomic positions derived from single-crystal and single-phase Rietveld refinements: (a) olivine; (b) pyroxene.

these differences are not statistically significant. The situation is the same for the pyroxene refinements (Table 7); the maximum differences are 0.021(8) Å for *M*1–O2 and 0.025(11) Å for *T*–O3b; as with the olivine, these differences are not statistically significant.

The situation for the multiphase Rietveld refinements is less satisfactory, particularly where the modal proportion of the phase is small. For the olivine, there is reasonable agreement between the single-crystal and single-phase refinement values and the results of the multiphase refinements where the modal proportion of olivine exceeds 30%. Below this value, the ordering of the bond lengths in terms of relative size is maintained, but large deviations occur, and these are significant where the modal proportion of olivine is 10%. Similar behavior also occurs for the pyroxene results, although because of the slightly larger standard deviations, the differences are not statistically significant. To summarize, reasonably accurate interatomic distances can be obtained from Rietveld refinements of mixtures of olivine and pyroxene. However, where the modal proportion of either phase becomes small, the assigned standard deviations become so large that the interatomic distances are of no use for crystal-chemical purposes.

The interatomic distances for the refinement of the 1:1 mixture at a series of different step-widths from 0.02 to 0.10° 2θ do not significantly differ from the single-crystal values with increasing step-width. This indicates that the larger step-widths (*i.e.*, up to 0.10° 2θ) do not lead to a loss of accuracy, at least in the 1:1 mixture.

CONCLUSIONS

Rietveld refinement of known binary mixtures of olivine and pyroxene have been used to determine the accuracy of the method for the determination of modal proportion and structural details of complex minerals in mixed powders. The following conclusions may be drawn:

(1) The modal proportions can be determined with an absolute accuracy of 0.9% absolute and 3.0% relative; this is within the level of the assigned precision.

(2) The refined modal proportions are independent of step width over the range 0.02–0.10° 2θ.

(3) Accurate unit-cell dimensions are obtained except where the phase is a relatively minor (≤ 10%) component of the mixture.

(4) Site populations (and bulk compositions) are accurate to within their assigned level of precision. Where the phase is a minor component (*i.e.*, <10%), the assigned precision can be large; however, where the components are major (≥10%), the site populations and bulk compositions can be determined accurately and precisely.

(5) The refinement procedure is less sensitive to stereochemical details (*i.e.*, atomic positions). Accurate values are obtained, but where the proportion of the phase is less than 30%, the standard deviations are too large for the atomic positions to be useful.

(6) Finally, we note that the above conclusions were obtained on a mixture of phases of similar X-ray absorption coefficients. For cases in which the X-ray absorption coefficients of the constituent phases are distinctly different (Bish & Post 1993), errors due to differential X-ray absorption can be significant.

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