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PREDICTION OF THE CRYSTAL-CHEMICAL COMPOSITION OF CLINOAMPHIBOLES FROM X-RAY INTENSITY MEASUREMENT OF SELECTED REFLECTIONS (*PREVEDI* COMPUTER PROGRAM)

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RIASSUNTO. — Un'analisi di regressione multipla stepwise applicata ai risultati del raffinamento cristallografico di 182 clino-anfiboli ha permesso di ottenere un insieme di equazioni che correlano le intensità di 100 riflessi con la pópolazione dei siti, le distanze medie di legame e l'eventuale sdoppiamento dei siti cationici. È stato quindi preparato un programma (chiamato PREVEDI) che trasforma i risultati dell'applicazione delle equazioni di regressione alle intensità di qualunque anfibolo in una formula cristallochimica. Con questa procedura si ottiene un modello cristallochimico assai vicino a quello corretto e utilizzabile senza ulteriori cambiamenti per il raffinamento cristallografico. È stata inoltre preparata una versione ridotta del programma che, utilizzando le intensità di solo 20 riflessi e i parametri c e β della cella elementare, riesce a dare una formula cristallochimica sufficientemente accurata per riconoscere variazioni cristallochimiche significative fra diversi cristalli della stessa roccia e scegliere quelli giudicati interessanti per un raffinamento cristallografico.

ABSTRACT. — Stepwise multiple regression analysis applied to crystallographic refinement results of 182 C2/m amphiboles has allowed to obtain a set of equations correlating the X-ray diffraction intensity of 100 reflections with site population, mean bond length and splitting features of the cationic sites. A simple computer program PREVEDI has been set up in order to transform the results of the regression equations into a crystal-chemical formula. In this way a crystal-chemical model close to the correct-one can be used without further changes in the course of the refinement process. A reduced version has been also set up which, using the X-ray intensities of only 20 reflections and the unit cell parameters c and β, can give a crystal-chemical formula of sufficient accuracy to recognize significant chemical variations among crystals of the same rock and to select those judged suitable for the crystallographic refinement.

Introduction

About two hundred structures of clinoamphiboles from rocks of peculiar petrographic and paragenetic interest and exhibiting wide chemical variations have been refined during the last four years at the Centro di Studio per la Cristallografia Strutturale (CSCS) of Pavia.

Data collection and refinement procedures have been optimized so that a good deal of crystal-chemical accuracy can be easily achieved (UNGARETTI, 1980): the final discrepancy index between observed and calculated structure factors ranges in all cases between 1.2 and 2.5 %; the e.s.d. of interatomic distances — which accounts not only for counting statistics but also for discrepancy in the measurement of equivalent reflections — is usually lower than 0.001 Å; the e.s.d. on the mean atomic number of the atomic species present in the cationic sites is always lower than 0.1 electrons.

The information obtained from X-ray refinements is elaborated by the computer program CORANF (UNGARETTI, SMITH and ROSSI, 1981; CANNILLO, OBERTI and UNGARETTI, 1981), which determines the crystal-chemical formula of the amphibole under investigation and calculates the correlations between chemical, geometric and crystallographic parameters for all the amphiboles so far refined.

As long as the number of investigated crystals increased, the need of a quick preventive estimate of the crystal-chemical composition of a new specimen became more and more crucial for two important and distinct reasons: *a*) to avoid to collect a complete set of X-ray diffraction data for amphiboles with crystal-chemical composi-

TABLE 1

Cation contents (in atoms per f.u.) from X-ray refinement for: a) *three amphiboles having similar unit cell volume,* b) *two amphiboles having similar unit cell dimensions*

a)

AMPHIBOLE NUMBER	V	K	Na	Ca	Mg	Fe	Al	Si
31	910.1	0.13	0.62	1.69	3.47	1.34	1.15	7.04
55	910.5		0.62	1.83	2.17	2.08	2.45	6.36
144	910.8	0.16	0.72	1.92	3.31	1.61	2.07	6.08

b)

AMPHIBOLE NUMBER	a	b	c	β	Na	Ca	Mg	Fe	Al	Si
47	9.84	18.05	5.30	105.0	0.32	1.83	3.70	1.25	1.20	7.02
116	9.83	18.02	5.31	105.1	0.57	1.88	3.01	1.54	2.19	6.37

Observed unit cell parameters variations in 182 amphiboles refined at the CSCS: $a = 9.50\text{-}10.03$ Å; $b = 17.70\text{-}18.20$ Å; $c = 5.27\text{-}5.36$ Å; $\beta = 103.5\text{-}105.5°$; $V = 869\text{-}935$ Å^3.

TABLE 2

Comparison between the cation contents (in atoms per f.u.) predicted by PREVEDI (P) and calculated by CORANF (C) at the end of the refinement for one alkali, one sodic-calcic and one calcic amphibole

AMPHIBOLE NUMBER		A		M4			M1 + M2 + M3				T	
		K	Na	Ca	Na	Fe	Mg	Fe^{2+}	Fe^{3+}	Al	Si	Al
62	P				2.00		1.13	1.87	0.24	1.76	8.00	
	C				○1.95		1.13	1.88	0.18	1.81	8.00	
140	P	0.91		1.05	0.95		○○4.91	0.02			8.00	
	C	0.80	0.14	1.01	0.99		○○○4.86	0.02	0.02	0.07	7.97	0.03
151	P	0.06	0.34	1.83		0.17	2.60	1.21	0.44	0.75	6.40	1.60
	C		0.47	1.84		0.16	2.50	1.40	0.19	0.90	6.44	1.56

○ +0.05 Li; ○○ +0.07 vacancy; ○○○ +0.03 vacancy.

tions very similar to others already obtained; *b*) to be able, if the diffraction data have been collected, to start the refinement procedure with a crystal-chemical model as much as possible close to the correct one, in order to save computing time and to avoid operator's interventions.

It must be pointed out that the atomic coordinates do not differ very much among the various isomorphous members of the C2/m amphibole family; moreover atomic coordinates always converge to the right values in a few cycles of least-squares refinement. On the contrary, the chemical composition of the cationic sites can differ very much in different amphibole crystals; this implies not only several cycles of refinement due to correlation among scattering power, thermal parameters, scale factor, secondary extinction correction, etc., but also several operator's interventions and some caution. In fact the initial choice of scattering factors often needs to be changed in some cationic sites, according to the observed bond lengths and to charge balance considerations. Moreover, only after inspecting a good-quality difference Fourier map, a clear picture of the positional disorder around the *M*4 and *A* sites (Hawthorne and Grundy, 1978; Bocchio, Ungaretti and Rossi, 1978) can be obtained and the required adjustements of the structural model have to be made before to continue the refinement process.

On the other hand, as confirmed from the structural refinements so far carried out at the CSCS of Pavia, chemical and structural informations cannot be directly obtained from the unit cell parameters. In fact in some cases, where a particular combination of isomorphous substitutions gives rise to contrasting geometric effects, large crystal-chemical differences do not correspond to significant variations in the unit cell parameters (see Table 1).

Therefore, the lack of crystal-chemical information compels to carry out a preliminary refinement, to elaborate the results so obtained, to modify accordingly the crystal-chemical model (e.g. by changing some atomic scattering factors, by including some split sites, etc.), and then to perform additional least-squares cycles. At the end of this quite labourious work, it may happen that the crystal-chemical composition so obtained was already present in the file of the refined clinoamphiboles.

Method

On the basis of previous experiences performed on blue amphiboles (Ungaretti, Dal Negro, Mazzi and Rossi, 1977), a more general treatment has been set up for predetermining in a simple way a reliable crystal-chemical composition of C2/m amphiboles from single-crystal X-ray diffraction measurements. The method is based upon the fact that the various isomorphous substitutions occurring in amphiboles determine large intensity changes only in a relatively small group of reflections. By comparing the diffraction data of 182 natural amphiboles with widely different crystal-chemical composition so far refined at CSCS, 150 reflections, characterized by strong intensity

TABLE 3

Observed intensity variation (on absolute scale) for 182 C2/m amphiboles of the 20 reflections used by PREVEDI to predict the chemical composition

h k l	$I_{min.}$	$I_{max.}$	I_{mean}
3 3 0	21600	63900	31100
2 4 0	39200	85200	58900
0 10 0	17400	98300	37100
-4 2 1	18500	56100	40000
-3 3 1	20900	89600	53900
3 5 1	24100	120100	62700
5 5 1	16800	59700	29800
-1 7 1	10600	54900	30100
-4 0 2	36700	178900	90000
-3 1 2	37900	139400	66300
-3 3 2	10400	44100	16700
4 4 2	11600	22500	14300
-2 8 2	15600	36200	24600
1 11 2	26900	75600	52300
0 12 2	11200	36100	21900
4 12 2	12500	26800	17900
0 0 4	23300	87600	42100
-1 1 4	28400	59200	39500
-1 11 4	17100	38800	25900
-2 0 6	10200	30000	17900

and by large intensity variations, have been selected.

A stepwise multiple regression (SMR) program has been employed in order to correlate the intensity of the selected reflections and the unit cell parameters with the mean atomic number and the mean bond length of each of the cationic sites *T*1, *M*1, *M*2, *M*3, *M*4 and *A*. It came out that 100 out of the 150 selected reflections were sufficient to give very high correlation coefficients for mean bond length and mean atomic number not only of the conventional sites, but also of the split sites *A, Am, A*2 and *M*4, *M*4′. In particular the intensities of 11 reflections were used to determine at high confidence level ($R = 0.997$) the mean atomic number of the *A*(tot) site, 24 reflections plus *b* and *V* for the *M*4(tot) site ($R = 0.999$), 9 reflections ($R = 0.997$) for *M*1, 13 reflections for *M*2 ($R = 0.997$), 10 reflections ($R = 0.994$) for *M*3, 7 reflections plus *c* ($R = 0.995$) for the Al content in the *T*1 site.

A simple computer program PREVEDI has been thereafter set up which applies on the diffraction data collected with the single crystal diffractometer the equations computed by the SMR, determines the crystal-chemical composition and indicates the kind and the relative proportions of the scattering factors to be used in the cationic sites. In this way a very reliable crystal-chemical model can be obtained and used without the need of modifying it in the course of the refinement.

TABLE 4

Regression equations relating the intensity (on absolute scale) of 20 selected reflections and unit cell dimensions to the crystal-chemical parameters

	n. el. in A_{tot}		n. el. in $M4_{tot}$		n. el. in M1	
	R = 0.983		R = 0.991		R = 0.980	
	C	A	C	A	C	A
I	-695.83714		-991.76224		13.97376	
II	6.63966	β	9.84706	β	0.00010	I(3 5 1)
III	-0.00008	I($\bar{3}$ 3 1)	-0.00038	I($\bar{3}$ 3 2)	0.00011	I(0 10 0)
IV	-0.00050	I($\bar{2}$ 8 2)	0.00083	I($\bar{2}$ 0 6)	0.00035	I($\bar{1}$ 1 4)
V	0.00090	I($\bar{3}$ 3 2)	-0.00031	I($\bar{1}$ 1 4)	-0.00026	I(0 12 2)
VI	0.00016	I(2 4 0)				

	n. el. in M2		n. el. in M3		Al in T1	
	R = 0.988		R = 0.980		R = 0.987	
	C	A	C	A	C	A
I	-799.48697		10.30331		-11.93523	
II	153.79409	c	0.00011	I(1 11 2)	0.11582	β
III	0.00008	I(0 0 4)	-0.00010	I($\bar{1}$ 7 1)	-0.00011	I(4 4 2)
IV	0.00032	I(3 3 0)	0.00018	I(5 5 1)	0.00006	I($\bar{1}$ 11 4)
V	0.00035	I($\bar{2}$ 8 2)	-0.00022	I($\bar{2}$ 8 2)	0.00003	I($\bar{4}$ 2 1)
VI	-0.00014	I($\bar{4}$ 2 1)	0.00025	I(4 12 2)	-0.00002	I($\bar{3}$ 1 2)
VII					0.00001	I($\bar{4}$ 0 2)

The equations are in the form: *Parameter* = $= C(\mathrm{I}) + C(\mathrm{II})A(\mathrm{II}) + \ldots C(N)A(N)$; *R* is the multiple correlation coefficient. *n.el.* = mean atomic number in electrons.

Table 2 shows the comparison between the crystal-chemical composition predicted by PREVEDI and that given by CORANF at the end of the refinement. As it can be seen the agreement is excellent and the refinement has very little modified the predetermined chemical composition.

However since a too large number (100) of reflections need to be measured to obtain a highly reliable chemical formula, reduced versions of the program PREVEDI have been tested, which use only 20 or 38 reflections. Of course these reduced versions are not able to predict fine-scale details like the presence of split *A* and *M*4 sites, but are of great usefulness in the preliminary steps, when several crystals belonging to the same rock are examined with the diffractometer. Significant crystal-chemical variations are easily detected by measuring the intensity of a small number of reflections. Moreover, deviations from the general behaviour shown by the C2/m amphiboles can also be assessed in this way: an example is illustrated in Fig. 1, where the number of electrons pre-

TABLE 5

Simplified crystal-chemical procedure used by PREVEDI to convert the crystal-chemical parameters of Table 4 into a crystal-chemical formula

A site	n.el. A	≤ 11	$\frac{\text{n.el. A}}{11}$	= Na
		> 11	$\frac{\text{n.el. A} - 11}{8}$	= K
			1 - K	= Na
M4 site	n.el. M4	≤ 40	$\frac{\text{n.el. M4} - 22}{9}$	= Ca
			2 - Ca	= Na
		> 40	$\frac{\text{n.el. M4} - 40}{6}$	= Fe^{2+}
			2 - Fe^{2+}	= Ca
M1 site			$\frac{\text{n.el. M1} - 24}{14}$	= Fe^{2+}
			2 - Fe^{2+}	= Mg
M3 site			$\frac{\text{n.el. M3} - 12}{14}$	= Fe^{2+}
			1 - Fe^{2+}	= Mg
M2 site			$\begin{cases} (\text{Mg})\,X + (Fe^{3+})\,Y + (\text{Al})\,Z = 2 \\ 12\,X + 26\,Y + 13\,Z = \text{n.el. M2} \\ 2\,X + 3\,Y + 3\,Z = \text{charge M2} \end{cases}$ where charge M2 = 14 + (Al in T1) - charge A - charge M4 - 6	
T1 site			4 - Al in T1 = Si	
T2 site			4 = Si	

TABLE 6

Comparison between the crystal-chemical formula of a C2/m amphibole elaborated by CORANF (c) *at the end of the refinement and that predicted by PREVEDI without* (a) *and with* (b) *absorption correction applied to the intensities of 20 reflections*

		(a)	(b)	(c)
A site	n.el.	4.474	5.397	4.829
	site pop.	$Na_{0.41}$	$Na_{0.49}$	$Na_{0.41}K_{0.02}$
M4 site	n.el.	38.690	40.771	40.666
	site pop.	$Ca_{1.85}Na_{0.15}$	$Ca_{1.87}Fe^{2+}_{0.13}$	$Ca_{1.89}Fe_{0.11}$
M1 site	n.el.	28.914	30.206	30.468
	site pop.	$Fe^{2+}_{0.35}Mg_{1.65}$	$Fe^{2+}_{0.44}Mg_{1.56}$	$Fe^{2+}_{0.46}Mg_{1.54}$
M2 site	n.el.	31.351	31.094	30.518
	site pop.	$Fe^{3+}_{0.46}Mg_{0.56}Al_{0.98}$	$Fe^{3+}_{0.48}Mg_{1.20}Al_{0.32}$	$Fe^{3+}_{0.40}Mg_{1.24}Al_{0.30}Ti_{0.06}$
M3 site	n.el.	14.450	15.688	16.186
	site pop.	$Fe^{2+}_{0.17}Mg_{0.83}$	$Fe^{2+}_{0.26}Mg_{0.74}$	$Fe^{2+}_{0.21}Fe^{3+}_{0.09}Mg_{0.70}$
T1	site pop.	$Al_{1.69}Si_{2.31}$	$Al_{1.30}Si_{2.70}$	$Al_{1.34}Si_{2.66}$

(a)	$Na_{0.41}$	$Ca_{1.85}Na_{0.15}$	$Fe^{2+}_{0.53}Fe^{3+}_{0.46}Mg_{3.04}Al_{0.98}$	$Al_{1.69}Si_{6.31}$	$O_{22}(OH)_2$
(b)	$Na_{0.49}$	$Ca_{1.87}Fe^{2+}_{0.13}$	$Fe^{2+}_{0.71}Fe^{3+}_{0.48}Mg_{3.49}Al_{0.32}$	$Al_{1.30}Si_{6.70}$	$O_{22}(OH)_2$
(c)	$Na_{0.41}K_{0.02}$	$Ca_{1.89}Fe^{2+}_{0.11}$	$Fe^{2+}_{0.67}Fe^{3+}_{0.49}Mg_{3.48}Al_{0.30}Ti_{0.06}$	$Al_{1.34}Si_{6.66}$	$O_{22}(OH)_2$

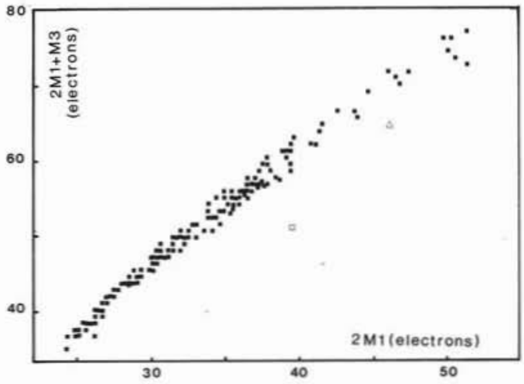

Fig. 1. — Number of electrons in the M1 site versus the total number of electrons in the (M1+M3) sites. The least squares equation, using 182 C2/m amphiboles is: 1.500 el. M1+1.180 = el. (M1+M3) (correlation coefficient $R = 0.991$). The open square refers to a twinned crystal; the triangle to a completely dehydrogenated riebeckite.

sent in $M1 + M3$ sites is plotted against the number of electrons in $M1$ (in the $M1$ and $M3$ sites of C2/m clinoamphiboles only Mg and Fe^{2+} are usually present). The correlation coefficient is very high for the 182 amphiboles so far refined at the CSCS and large deviations from the general trend have to be cautiously considered being due or to dehydrogenation fenomena (UNGARETTI, 1980) or to the presence of strange crystallographic features which need to be examined in details before starting the data collection. In fact the refinement of the crystal represented with the open square in Fig. 1 did not converge and gave an unaccettable R value ($\sim 25\ \%$); a further examination of this sample revealed twinning features which are now under investigation.

Conclusions

Multiple regression analysis applied to X-ray intensities diffracted by amphibole single crystals has shown high correlation coefficients with the more important crystal-chemical parameters. Linear equations based upon the unit cell dimensions and the intensity of 100 strong reflections give, with high confidence level, mean bond lengths and atomic scattering powers of the cationic sites. This information is easily transformed by the computer program PREVEDI into a crystal-chemical formula very similar to that obtained by a complete crystallographic refinement (tables of coefficients of the complete set of equations are available upon request from the Authors). Additionally the computer program PREVEDI gives a reliable and detailed crystal-chemical model which can be used since the beginning in the crystallographic refinement.

A reduced version has been also set up which uses the intensities of 20 reflections (see Table 3) for a preliminary rough estimate of the crystal-chemical composition of any C2/m amphibole. This reduced version is particularly suitable for an immediate check of the chemical composition of an amphibole and to select the crystals whose chemical composition worths to be studied in more details by a complete crystallographic refinement. The program can operate directly on the computer which controls the single-crystal diffractometer in such a way that, once the unit cell dimensions have been measured, a quick collection of the selected reflections can be carried out and the intensity values can be immediately elaborated to give the crystal-chemical composition.

In particular 3 reflections are used to put the intensities on the absolute scale K, following the equation: $K = 37100/[I\ (442) + I\ (533) + I\ (\bar{1}34)]$; then six linear regression equations (see Table 4) give respectively the tetrahedral Al content (in atoms per f.u.), and the scattering power (in electrons) for the A, $M4$, $M1$, $M2$ and $M3$ sites. A simplified crystal-chemical procedure, in respect to that used by CORANF (see Table 5), has been adopted to transform the values given by the regression equations into a chemical unit formula in terms of the major elements which can be present in an amphibole. To enhance the accuracy level, an absorption correction based upon the method of NORTH, PHILLIPS and MATHEWS (1968) can be easily applied.

A comparison between the refinement results elaborated by CORANF and those given by the reduced version of the PREVEDI program (using 20 reflections), either corrected or not for absorption, is reported in Table 6. The example shown refers to a crystal having relatively high shape absorption coefficient (maximum value of $K_{\text{abs.}} = 1.40$); the predicted crystal-chemical composition is in this case significantly affected by the inclusion of absorption correction, which determines large intensity changes. Actually the crystallographic refinement, based upon 1083 reflections (final conventional discrepancy factor $R = 1.42\%$) has only slightly modified the chemical composition predicted by PREVEDI by using the intensity, corrected for shape absorption, of 20 reflections.

As soon as additional crystallographic refinement will be carried out, their inclusion in the multiple regression analysis should enhance even more the accuracy and the completness of the prediction made by PREVEDI both in its largest and reduced version.

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