

A CRYSTAL-CHEMICAL STUDY ON SIX FASSAITES FROM THE PREDAZZO-MONZONI AREA

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RIASSUNTO. — Allo scopo di indagare l'influenza della presenza di Al^{IV} sulla geometria dei siti tetraedrici ed ottaedrici dei clinopirosseni, è stato intrapreso uno studio cristallografico mediante diffrattometria a cristallo singolo su sei fassaiti a diverso tenore di Al^{IV} provenienti dalla zona Predazzo-Monzoni. La serie di campioni si presenta particolarmente interessante in quanto il sito $M2$ risulta quasi completamente occupato da Ca ed il contenuto di Ti è estremamente basso. I risultati dei raffinamenti cristallografici, terminati con fattori di discordanza compresi fra 1,2 e 1,9%, per i riflessi con $I > 3\sigma(I)$, e delle analisi con la microsonda elettronica eseguite sugli stessi cristalli usati per le riprese, permettono di trarre alcune interessanti conclusioni: per quanto riguarda il sito tetraedrico, viene proposta una nuova relazione per il calcolo del contenuto di Al^{IV} ; per quanto riguarda il sito $M1$, sembra di poter concludere che la presenza di Al^{IV} induca delle deformazioni anche nello strato ottaedrico: vengono quindi proposte nuove distanze per gli « end-members » utilizzabili per il calcolo della composizione di $M1$ nel caso di clinopirosseni contenenti Al^{IV} .

ABSTRACT. — In order to evaluate the consequences of the Si- Al^{IV} substitution in clinopyroxenes, a crystal-chemical study by single crystal X-ray diffractometry of six fassaites from the Predazzo-Monzoni area has been undertaken.

The crystallographic refinement yielded agreement factors between 0.012 and 0.019. Some considerations on the geometrical alterations of the tetrahedral and octahedral sites are reported, together with a new equation which allows to evaluate the Al^{IV} content in Ca-clinopyroxenes.

Introduction

Fassaites are Al^{IV} -rich clinopyroxenes, space group $C2/c$, which are particularly suitable for the investigation of the influence of the Si- Al^{IV} substitution in the geometrical features of the tetrahedral and octahedral sites. They present the peculiarity that the

$M2$ site is almost completely filled with Ca, with negligible amounts of Na and $Fe^{2+} + Mg$. Therefore the geometry of the tetrahedral and octahedral sites is not affected by changes in the population of the eight-coordinated site.

Few and heterogeneous crystal-chemical data on fassaites were up to now available: among the three specimens reported so far, only one was of terrestrial origin (PEACOR, 1967); one of the remaining (DOWTY and CLARK, 1973) is particularly rich of titanium (0.5 atoms per f.u.).

Six fassaite specimens were selected, owing to their homogeneously increasing Al^{IV} content, among those available in the Istituto di Mineralogia of Bologna, coming from the triassic calcareous and dolomitic rocks thermally metamorphosed at the contact with the dioritic intrusion of Monti Monzoni, Val di Fiemme, Italy. Their mineralogical characterizations have been throughout reported elsewhere (MINGUZZI et al., 1976) and the labels of the samples have been maintained in this work. All the specimens have a low Ti^{4+} content and are therefore an almost ideal set of samples for a crystal-chemical study of the solid solutions of diopside and hedenbergite with the Al- and Fe^{3+} -Ca-Tschermak pyroxenes.

Experimental

A) X-ray single crystal diffractometry

The data collections were performed for the six specimens on a Philips PW 1100 four-circle diffractometer in the θ range 2-30°. $MoK\alpha$ graphite monochromatized radiation

TABLE I
Selected crystal data

Sample	\underline{a} (Å) ±0.001	\underline{b} (Å) ±0.001	\underline{c} (Å) ±0.001	β (°) ±0.01	\underline{V} (Å ³)	n. of I(obs) I>3σ(I)	n. of I(meas)	R_{sym} x100	R_{obs} x100	R_{all} x100	ext. coef. x1000
062/02	9.741	8.893	5.268	105.88	438.93	576	648	1.40	1.26	1.67	0.167
056/01	9.748	8.895	5.274	105.87	439.86	594	647	//	1.76	2.16	0.430
054/02	9.738	8.879	5.278	105.91	438.87	592	647	1.20	1.24	1.51	0.083
071/04	9.742	8.880	5.283	105.80	439.76	593	649	2.80	1.45	1.65	1.467
072/03	9.734	8.859	5.286	105.94	438.29	590	645	1.80	1.41	1.66	1.004
071/01	9.746	8.854	5.300	105.93	439.77	595	647	//	1.89	2.13	0.240

R_{sym} refers to the agreement between the intensity measurements of equivalent reflections and is expressed as:

$$\sum_{hkl} \sum_{i=1}^N |I(bkl)_i - \bar{I}(bkl)| / \sum_{hkl} \sum_{i=1}^N I(bkl)_i$$

where $I(bkl)_i$ is the i^{th} measurement of the reflection bkl and $\bar{I}(bkl)$ is the mean value of the N equivalent reflections, R_{obs} and R_{all} are the final conventional discrepancy indices expressed as:

$$\sum |F_o| - |F_c| / \sum F_o$$

was used. The ω -scan technique was employed and two equivalent monoclinic reflections were collected, except for 056/01 and 071/01.

Unit cell dimensions were measured using the standard PW 1100 LAT routine. Intensities were corrected for Lorentz and polarization factors so as for absorption following the method of NORTH et al. (1968) and then merged. Technical details are given in Table 1.

The refinements have been carried out without chemical constraints with the full-matrix least-squares method using a locally modified version of the program ORFLS (BUSING et al., 1962): only reflections with $I > 3 \sigma(I)$ were regarded as observed. The initial atomic coordinates were those of diopside (SASAKI et al., 1980). Ionized scattering factors (International Tables for X-ray Crystallography, 1974; TOKONAMI et al., 1965) were used; during the refinement it was assumed that the M1 site was occupied only by Fe^{2+} and Mg^{2+} ; as for the M2 site, Ca^{2+} and Na^+ were considered at the beginning: Fe^{2+} was then substituted for Na^+

when the number of electrons turned out to be greater than 20.0.

As for the tetrahedron, partially ionized scattering factors were used: 1.5 positive charges were assumed for Si and 1.5 negative charges for O (ROSSI et al., 1983). The refinement of the occupancy factors was performed with the constraint of the full occupancy of the site. The Al^{IV} content was calculated after the isotropic refinement, starting from the average $T-O$ bond distance, according to the equation: $(\langle T-O \rangle - 1.634)/0.117 = \text{Al}^{\text{IV}}$ (a.f.u.) (HAZEN and FINGER, 1977) and was kept fixed in the anisotropic refinement. All the parameters were varied simultaneously: no correlation greater than 0.6 was observed. Also the secondary extinction coefficient (COPPENS and HAMILTON, 1970) was allowed to vary.

A final Fourier difference map did not reveal relevant peaks besides those midway between the silicon and the non bridging oxygens.

The agreement factors after the anisotropic refinement are reported in Table 1. Atomic coordinates, isotropic equivalent temperature factors and various geometrical pa-

TABLE 2
*Positional parameters ($\times 10^4$) and thermal isotropic equivalent factors
 for the six fassaite crystals*
 The maximum value of e.s.d. is 0.0002

Sample	Atom	x/a	y/b	z/c	$B_{eq.}$	Sample	Atom	x/a	y/b	z/c	$B_{eq.}$
062/02	T	2866	934	2277	0.34	071/04	T	2870	934	2268	0.33
	01	1145	871	1399	0.54		01	1138	869	1386	0.57
	02	3615	2516	3187	0.68		02	3620	2531	3192	0.73
	03	3512	181	- 67	0.61		03	3518	186	- 75	0.66
	M1	0	9080	2500	0.43		M1	0	9072	2500	0.41
	M2	0	3028	2500	0.65		M2	0	3037	2500	0.63
056/01	T	2867	934	2278	0.37	072/03	T	2869	935	2259	0.38
	01	1143	870	1402	0.56		01	1130	867	1372	0.64
	02	3613	2521	3189	0.70		02	3620	2540	3187	0.75
	03	3514	183	- 67	0.64		03	3520	187	- 86	0.67
	M1	0	9075	2500	0.43		M1	0	9076	2500	0.42
	M2	0	3029	2500	0.65		M2	0	3042	2500	0.68
054/02	T	2868	935	2268	0.36	071/01	T	2873	934	2259	0.34
	01	1137	868	1386	0.58		01	1129	869	1372	0.63
	02	3617	2530	3185	0.74		02	3621	2547	3189	0.76
	03	3517	183	- 74	0.66		03	3523	190	- 88	0.67
	M1	0	9076	2500	0.44		M1	0	9068	2500	0.36
	M2	0	3035	2500	0.66		M2	0	3050	2500	0.63

rameters are reported in Tables 2 and 3.

Lists of observed and calculated structure factors and of anisotropic thermal parameters are available on request from one of the authors (R.O.).

B) Electron microprobe analyses

The averaged chemical analyses and atomic formulae of fassaites are reported in Table 4.

The same crystal used for X-ray data collection was analyzed by the electron microprobe. The analyses were carried out in the wavelength dispersive mode on a fully automated ARL-SEM-Q instrument operated at 15 kv, 0.2 μ A beam current. On-line data reduction was based on the ZIEBOLD and OGILVIE method (1964) by the use of ALBEE and RAY correction factors (1970).

The agreement between X-ray and electron microprobe results is quite satisfactory: the number of electrons in the M1 and M2 sites obtained independently from X-ray refine-

ment and from EMP analyses are reported in Table 5. This concordance is a reliable starting point for the crystal-chemical discussion.

Discussion

A) The T site

The linear relationship between T-O distances and Al^{IV} content in pyroxenes whose M2 sites are almost filled with Ca is nowadays a common knowledge. HAZEN and FINGER (1977) suggested three equations for T-O bridging, non-bridging and mean distances respectively (Table 6); they were calculated on the basis of the old crystallographic refinement of diopside (CLARK et al., 1969), of the Quebec fassaite (PEACOR, 1967) and of the Ti-rich Allende fassaite (DOWTY and CLARK, 1973).

By using the Al^{IV} percentages from EMP analyses and the T-O distances from the

TABLE 3
Geometrical parameters from X-ray refinement
Standard deviations in parentheses

	062/02	056/01	054/02	071/04	072/03	071/01
T-01	1.6131(8)	1.6170(6)	1.6222(8)	1.6248(11)	1.6289(9)	1.6353(14)
-02	1.5971(9)	1.6004(6)	1.6057(9)	1.6086(12)	1.6121(10)	1.6176(15)
-03A1	1.6718(8)	1.6733(6)	1.6739(8)	1.6731(11)	1.6763(9)	1.6781(14)
-03A2	1.6899(8)	1.6916(6)	1.6932(8)	1.6954(11)	1.6941(10)	1.6971(14)
Average	1.6430	1.6456	1.6488	1.6505	1.6528	1.6570
TQE	1.0065	1.0064	1.0064	1.0064	1.0064	1.0061
TAV	27.65	26.96	27.35	27.37	27.17	26.00
TILT	2.43	2.36	2.34	2.41	2.35	2.32
T-03-TA2	135.74(5)	135.70(4)	135.61(5)	135.65(7)	135.52(6)	135.53(9)
03A2-03A1-03A2	166.06(7)	165.95(5)	165.92(7)	165.76(9)	165.72(8)	165.53(11)
M1-01A1,B1	2.1147(8)	2.1168(6)	2.1119(8)	2.1158(11)	2.1080(10)	2.1146(14)
-01A2,B2	2.0520(7)	2.0554(5)	2.0470(7)	2.0511(10)	2.0409(9)	2.0458(13)
-02C1,D1	2.0378(9)	2.0345(6)	2.0240(9)	2.0206(12)	2.0139(10)	2.0053(14)
Average	2.0681	2.0689	2.0609	2.0625	2.0543	2.0552
Vo1	11.694	11.703	11.563	11.588	11.443	11.453
OQE	1.0060	1.0062	1.0066	1.0067	1.0071	1.0076
OAV	19.29	20.00	21.17	21.30	22.49	23.74
M2-01A1,B1	2.3694(8)	2.3709(6)	2.3732(8)	2.3742(11)	2.3740(9)	2.3790(14)
-02C2,D2	2.3536(8)	2.3570(6)	2.3602(8)	2.3611(11)	2.3635(9)	2.3709(13)
-03C1,D1	2.5540(8)	2.5549(6)	2.5483(8)	2.5506(11)	2.5443(10)	2.5414(14)
-03C2,D2	2.7013(8)	2.7003(6)	2.6905(8)	2.6875(11)	2.6788(9)	2.6729(13)
Average	2.4946	2.4958	2.4930	2.4934	2.4902	2.4911
Vo1	25.682	25.732	25.648	25.663	25.572	25.629

TQE = Tetrahedral quadratic elongation (ROBINSON et al., 1971); TAV = Tetrahedral angle variance (ROBINSON et al., 1971); TILT = Out-of-plane tilting of the basal face of the tetrahedron (CAMERON et al., 1973); OQE = Octahedral quadratic elongation (ROBINSON et al., 1971).

crystallographic refinements of five samples of fassaite, together with the new distances for diopside from a X-ray refinement at 0.4 Å resolution (ROSSI et al., 1982), new coefficients were found for those relationships. They seem to be more reliable due to the accuracy of the refinements, to the homogeneity of the samples and to the fact that no interferences of unusual (e.g. Ti) elements are present. The change in the slope of the straight lines trends always towards the parameters reported for Ca-Ts (OKAMURA et al., 1974), even if its mean bridging T-O distance is much shorter than expected (fig. 1). This fact may be explained in terms of short range Al-Si ordering (GROVE and BURNHAM, 1974). A minor dispersion due to the heterogeneity of samples is present along the T-O mean straight line. Therefore,

it is probably reasonable to use this equation to evaluate the Al^{IV} content in samples which are not in the very conditions in which the plot has been set up. The relationship between T-O non bridging and Al^{IV} may be more profitably used especially for samples with a low Al^{IV} content. However, the evaluations of Al^{IV} content for the specimen which had not been probed varied from 0.092 (T-O mean) and 0.096 (T-O non bridging) atoms per tetrahedron. It must be pointed out that these equations hold only for Ca clinopyroxenes.

Correlations between cell parameters or combinations of cell parameters and Al^{IV} content were thereafter investigated. The best results were obtained with the relationship between $b/c \sin \beta$ vs. Al^{IV} (fig. 2): this one can be very useful for the determination

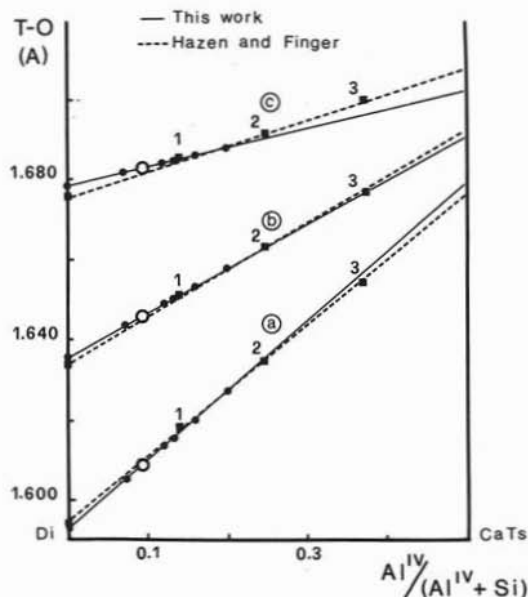


Fig. 1. — T-O non bridging (a), mean (b) and bridging (c) distances vs. Al^{IV} content per one tetrahedron for clinopyroxenes along the join diopside-CaTs. Black circles refer to the fassaite and diopside samples used to calculate the regression line; open circles refer to sample 056/01. Squares refer to samples reported in the literature: 1 = HAZEN and FINGER (1977); 2 = PEACOR (1967); 3 = DOWTY and CLARK (1973).

of the Al^{IV} content in a crystal without or before collecting X-ray diffraction data. Cell parameters may be in fact easily measured in any laboratory. This relationship holds also for the fassaite samples in the literature (which were not used for the calculation of the coefficients). The Quebec fassaite deviates from the line; its cell parameters were however determined some years ago on the basis of 0-level Weissenberg photographs and cannot therefore be considered accurate.

B) The M1 site

It has not been possible to determine the site population of the M1 sites by using the M1-O average bond distances of octahedra containing Al, Mg, Fe^{2+} and Fe^{3+} of the common end-member pyroxenes. As a matter of fact, the Al-O mean distance in CaTs (1.947 Å) is much larger than the corresponding one in jadeite (1.929 Å).

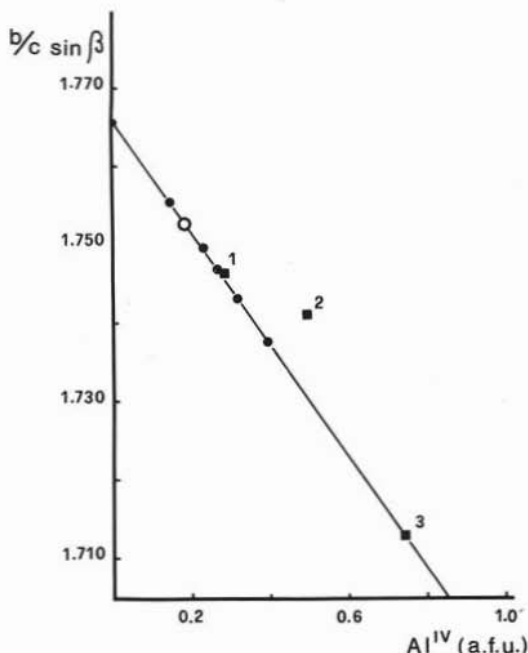


Fig. 2. — The best correlation found between a combination of cell parameters and Al^{IV} contents in the tetrahedra. The use of symbols is the same as in fig. 1. The equation is: $b/c \sin \beta = 1.766 - 0.072 Al^{IV}$.

However, even if the M1-O average distance of Al in CaTs and of Fe^{3+} in Fe^{3+} -CaTs (GHOSE et al., 1975; deduced on the basis of cell parameters) are used together with those of Mg in diopside and of Fe^{2+} in hedenbergite, the usual procedure of deriving the M1 site population from the number of electrons and from bond lengths considerations (see below), proved to be unsuccessful. The possible explanation is that the dimensions of the M1 octahedron in fassaites are not a linear function of its site population. This hypothesis is supported by the fact that the OQE of M1 is correlated more strongly ($R = 0.999$) to Al^{IV} than to the Mg content in the octahedron ($R = 0.971$). This fact means that the distortion produced by Al^{IV} in the octahedron obscures in some way the correlation between bond lengths and site population.

Founding on the agreement between the number of electrons in the M1 site from the two kinds of analyses, a system of five equations of the type:

TABLE 4

Chemical analyses and site populations based on six oxygens from electron microprobe data

		062/02	054/02	071/04	072/03	071/01
SiO ₂		50.25	47.33	46.39	45.37	42.43
TiO ₂		0.08	0.13	0.19	0.58	0.78
Al ₂ O ₃		5.42	9.68	8.79	11.17	11.61
Cr ₂ O ₃		0.00	0.03	0.11	0.00	0.03
Fe ₂ O ₃ ^a		1.69	1.39	4.79	3.97	8.43
FeO ^a		1.20	2.87	3.17	1.03	1.74
MnO		0.04	0.03	0.12	0.00	0.11
MgO		15.29	12.81	11.70	12.14	10.10
CaO		24.72	24.11	24.48	25.06	24.65
Na ₂ O		0.00	0.02	0.03	0.00	0.00
TOTAL		98.69	98.40	99.77	99.32	99.88
T	Si	1.856	1.764	1.733	1.684	1.600
	Al	0.144	0.236	0.267	0.316	0.400
M1	Mg ²⁺	0.842	0.712	0.651	0.672	0.568
	Fe ²⁺	0.015	0.053	0.081	0.029	0.051
	Al ³⁺	0.092	0.190	0.120	0.173	0.116
	Fe ³⁺	0.047	0.039	0.135	0.111	0.239
	Mn ²⁺	0.001	0.001	0.004	0.000	0.004
	Ti ⁴⁺	0.002	0.004	0.005	0.016	0.022
	Cr ³⁺	0.000	0.001	0.003	0.000	0.001
M2	Ca ²⁺	0.978	0.963	0.980	0.997	0.996
	Na ⁺	0.000	0.001	0.002	0.000	0.000
	Fe ²⁺	0.022	0.036	0.018	0.003	0.004

^a = Total Fe as FeO partitioned according to PAPIKE et al. (1974).

$A_1^i X_1 + A_2^i X_2 + A_3^i X_3 + A_4^i X_4 = D_{obs}^i$, has been tentatively set up, in which A_N^i are the known fractional quantities of Fe²⁺, Fe³⁺, Mg²⁺ and Al³⁺ in the M1 site, D_{obs}^i are the mean M1-O distances from the X-ray refinement for the i^{th} specimen and X_N are the unknown values for the M1-O mean distances of the hypothetical pyroxenes containing only the above mentioned cations. The small quantities of Ti⁴⁺, Cr³⁺ and Mn²⁺ from EMP analyses were considered together with Fe³⁺. The following M1-O mean distances were obtained:

$$\begin{aligned} Al^{3+} &= 1.9565 \text{ \AA} & Fe^{2+} &= 2.1666 \text{ \AA} \\ Fe^{3+} &= 2.0163 \text{ \AA} & Mg^{2+} &= 2.0814 \text{ \AA} \end{aligned}$$

The results, together with the condition of the full occupancy of the site, of charge

TABLE 5

Comparison between X-ray refinements and electron microprobe analyses

SAMPLE	N. OF ELECT. IN M1		N. OF ELECT. IN M2	
	X-RAY	EMP	X-RAY	EMP
062/02	13.26	13.00	20.16	20.13
054/02	14.04	13.54	20.20	20.21
071/04	15.29	15.29	20.09	20.08
072/03	14.21	14.28	20.20	20.02
071/01	16.16	16.45	20.06	20.02

TABLE 6

Coefficients of the regression equations and multiple correlation coefficients for the relationships between T-O bond distances and Al^{IV} content

T-O _{non bridging}	T.W.	Y = 1.593 + 0.171 X	R = 0.999
	H.F.	Y = 1.594 + 0.163 X	R = 0.999
T-O _{mean}	T.W.	Y = 1.635 + 0.110 X	R = 0.999
	H.F.	Y = 1.634 + 0.117 X	R = 1.000
T-O _{bridging}	T.W.	Y = 1.678 + 0.049 X	R = 0.998
	H.F.	Y = 1.675 + 0.065 X	R = 0.997

H.F. = HAZEN and FINGER (1977); T.W. = this work.

balance and of the number of electrons in the M1 site may be used to calculate the M1 site population of other Ca-pyroxenes containing Al^{IV}. The system of equations to be solved is:

$$\begin{cases} X + Y + Z + W = 1 \\ Y + W = Al^{IV} \\ 26X + 26Y + 12Z + 13W = Z_{M1} \\ 2.1666X + 2.0163Y + 2.0184Z + 1.9565W = M1-O \end{cases}$$

were Z_{M1} is the number of electrons in the M1 site obtained from the X-ray refinement, Al^{IV} is evaluated from the relationship between the T-O non bridging distance and Al^{IV} content, and X, Y, Z, W are the fractional occupancies of Fe²⁺, Fe³⁺, Mg²⁺ and Al³⁺ respectively.

It is appropriate to remember that those results may be useful only for the crystal-chemical study of a particular class of pyroxenes, in which a similar pattern of chemical substitutions and geometrical distortions can be recognised. However, it is quite reasonable that, in some cases, the features of a solid solution may not be a linear combination of the corresponding

ones of the end member components.

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