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CRYSTAL CHEMICAL STUDY  
OF ECLOGITIC AMPHIBOLES FROM ALPE ARAMI,  
LEPONTINE ALPS, SOUTHERN SWITZERLAND

RIASSUNTO. — Sono stati studiati mediante diffrattometro automatico a cristallo singolo alcuni anfiboli di differente colorazione (da verde a bruna) presenti in un'eclogite proveniente dal bordo settentrionale della peridotite granatifera affiorante a NW dell'Alpe Arami, presso Gorduno (Bellinzona). La determinazione dei parametri di cella, effettuata su 8 cristalli verdi e su 5 bruni, ha evidenziato piccole ma significative variazioni; in particolare sono stati misurati valori compresi entro i seguenti limiti:  $a = 9,818-9,851$ ,  $b = 17,947-17,992$ ,  $c = 5,289-5,307$  (Å);  $\beta = 104,89^{\circ}-105,14^{\circ}$ ;  $V = 902,3-907,6$  (Å<sup>3</sup>). Non è stata riscontrata nessuna correlazione fra parametri di cella e colore. Su tre dei cristalli esaminati sono stati eseguiti dei raffinamenti cristallografici che hanno condotto ad una loro dettagliata caratterizzazione cristallografica. Analisi eseguite in microsonda hanno mostrato significative variazioni di composizione chimica sia fra differenti cristalli che all'interno di ciascuno di essi. Le caratteristiche cristallografiche dei tre anfiboli sottoposti a raffinamento cristallografico, tutti riconducibili a delle *pargasiti*, fanno ritenere che le lenti eclogitiche dell'Alpe Arami abbiano iniziato il processo di anfibolitizzazione in condizioni di relativamente alto grado metamorfico (600-650° C e 6-7 kbars) e che condizioni di equilibrio non si siano potute raggiungere.

ABSTRACT. — Some eclogitic amphiboles from a lens at the border of the peridotitic mass of Gorduno (Alpe Arami, Bellinzona, Switzerland) have been studied by means of single crystal diffractometry. Unit cell parameter determinations, made on 13 crystals characterized by different colours (8 green and 5 brown crystals), have shown small but significant differences. In particular, the following ranges in unit cell constants have been observed:  $a = 9.818-9.851$ ,  $b = 17.947-17.992$ ,  $c = 5.289-5.307$  (Å);  $\beta = 104.89^{\circ}-105.14^{\circ}$ ;  $V = 902.3-907.6$  (Å<sup>3</sup>). No relationship has been found between cell parameters and colour of the crystals. Three out of the 13 crystals have been used for X-ray crystal structure refinements, obtaining a detailed crystal chemical characterization. Microprobe analyses have shown significant chemical variations both among different grains and different zones within each grain. The crystal chemical features of the refined eclogitic amphiboles, which can be considered as *pargasitic* terms, suggest that eclogitic lenses from Alpe Arami were beginning to convert into amphibolites under relatively high-grade metamorphic conditions (600-650° C, 6-7 kbars) and that equilibrium conditions were not reached.

Introduction

Chemical and physical properties of two calcic amphiboles occurring in an eclogite (70-AM-10) from a lens at the border of the peridotitic mass of Alpe

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Arami near Gorduno, Bellinzona (Switz.) have been described in a previous paper (BOCCHIO, 1977). On the basis of the features observed in thin section, the hypothesis was made that one of the amphiboles belonged to the primary assemblage of the eclogite, together with garnet, omphacite, rutile and kyanite. The other one was considered to be secondary and to represent a transformation product of the garnet during the lower pressure and temperature phase of the retrogressive metamorphism undergone by all the eclogites of the zone around Gorduno (BOCCHIO, 1975, 1977).

TABLE 1  
*Unit cell parameters of pargasites from eclogite 70-AM-10*

Crystal	a (Å)	b (Å)	c (Å)	$\beta$ (°)	V (Å <sup>3</sup> )	c sen $\beta$ /b	colour
1	9.836	17.956	5.289	105.01	902.3	0.28450	brown
2*	9.818	17.972	5.300	104.89	903.8	0.28500	green
3	9.845	17.947	5.306	105.08	905.2	0.28547	brown
4	9.835	17.986	5.296	104.89	905.4	0.28456	green
5*	9.851	17.981	5.293	105.04	905.4	0.28428	green
6	9.845	17.956	5.305	105.09	905.5	0.28526	green
7	9.843	17.967	5.302	105.03	905.6	0.28500	green
8	9.841	17.972	5.302	105.05	905.6	0.28490	brown
9	9.842	17.958	5.307	105.10	905.6	0.28532	pale green
10*	9.848	17.979	5.299	105.06	906.0	0.28461	brown
11	9.847	17.983	5.305	105.14	906.8	0.28476	brown
12	9.850	17.992	5.298	104.93	907.2	0.28452	green
13	9.849	17.990	5.304	105.03	907.6	0.28474	green
Average	9.842	17.972	5.300	105.03	905.5	0.28481	
Powder method	9.845(4)	17.987(7)	5.303(2)	105.11(03)	906.6	0.28463	

The numbers marked by an asterisk refer to the crystals used for X-ray structure refinement.

The chemical analyses, carried out by means of electron microprobe, showed remarkable differences even if the two amphiboles could be classified as pargasitic terms. In particular the «primary» amphibole, characterized by  $Al^{VI} > 1$  and  $Al^{IV} > 2$  was named «alumino ferroanpargasite». Owing to this rather unusual chemical composition and to the petrographic and chemical differences observed in the two amphiboles, it seemed of interest to make unit cell parameters determinations and crystal structure refinements by means of single crystal X-ray diffractometry.

### Cell parameters determination

It was possible to distinguish, in the amphibolic concentrate prepared from the crushed rock, grains of amphibole with colours ranging from green to brown. Considering also the features observed in thin section, it was assumed that the

green crystal corresponded to the «primary» amphibole and the brown to the «secondary» one. The cell parameters of two grains picked up from the two populations described above were determined by means of single crystal diffractometer (Bocchio, 1977).

The cell parameters of the two crystals were significantly different, but the differences were smaller than those expected on the basis of the two chemical analyses. Thus, in order to test the existence of two populations of unit cell parameters, 8 green and 5 brown crystals were selected and their lattice parameters measured. The results are given in table 1.

As one can see, the colours which mark the eclogitic amphiboles in thin section and in hand specimens show no relationship either with lattice parameters or, as

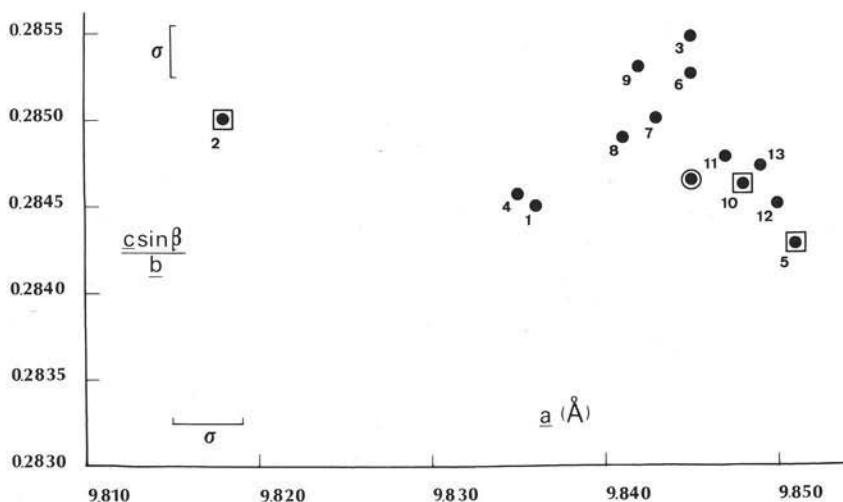


Fig. 1. —  $c \sin \beta / b$  versus  $a$  plot for amphiboles from 70-AM-10 eclogite. Circle: value obtained by powder method; squares: crystals used for crystallographic refinements.

will be discussed hereinafter in detail, with major chemical elements (Si, Al, Fe, Mg, Ca, Na). However the differences existing in the unit cell parameters of the 13 grains listed in table 1 are significant and should correspond to significant crystal chemical differences.

The errors affecting the lattice parameters determined by single crystal diffractometry may be considered to be roughly the same as those determined by the powder method, though the different features of the crystals (shape, size, quality of diffraction, etc.) might have an influence which cannot be easily controlled. However, the largest variations in each cell parameter range from 6 to 9 times the standard deviation determined with the powder method, i.e. they are surely significant.

The plot of  $c \sin \beta / b$  versus  $a$  (fig. 1) shows that the values tend to group around that obtained from the powder method; only sample No. 2 is significantly outside the cluster of the other points.

The conclusions which can be drawn from this preliminary approach are:

- 1) the most examined amphibole grains are characterized by unit cell parameters significantly different from those measured by means of the powder method;
- 2) the average cell parameters of the 13 crystals are nearly identical to those obtained by the powder method;
- 3) the differences in the lattice constants, even if significant, are smaller than those expected from the differences observed in the microprobe chemical analyses;
- 4) it is not possible to distinguish, on the basis of the unit cell parameters, two populations connected respectively with the «primary» and the «secondary» amphibole; at the most, sample No. 2 might have crystal chemical features in some way different from those of the other samples, owing to its peculiar position in the plot of fig. 1.

It is theoretically possible, however, that chemically different amphiboles have similar unit cell parameters, because of the multiple isomorphous replacements involving atoms which have opposite effects on the cell constants. To check this possibility, X-ray crystal structure analyses have been undertaken.

The crystals No. 2, No. 5, No. 10 of table 1 were selected for this purpose both for their position in the plot of fig. 1 and for the good quality of their diffraction spectra.

### X-ray data collection

X-ray data collection has been made using a single crystal automatic diffractometer Philips PW 1100 with MoK $\alpha$  radiation monochromatized by a flat graphite crystal.

The intensities of the reflections with  $2\theta \leq 60^\circ$  were collected using the  $\omega$ -scan mode; the equivalent pairs  $hkl$  and  $\bar{h}\bar{k}\bar{l}$  were scanned. Three standard reflections were monitored at four-hours intervals in order to check the orientation of the crystal and the intensity of the X-ray beam. No variation greater than 3% was observed for the intensity of the standard reflections of the three crystals.

The intensities were corrected for absorption following the method of NORTH et al. (1968) and the values of the equivalent pairs were averaged. The resulting discrepancy factors  $R_{\text{sym}} = \sum_{hkl} (I_{hkl} - \bar{I}) / \sum_{hkl} \bar{I}$ , where  $\bar{I} = (I_{h\bar{k}l} + I_{hkl})/2$ , were always less than 0.02.

The X-ray data were processed with a program specifically written for the PW 1100 diffractometer (HORNSTRA and STUBBE, 1972).

### X-ray structure refinements

The three structure refinements were carried out in space group C2/m with the atomic parameters of tremolite (PAPIKE et al., 1969). A locally rewritten version of the full matrix least-squares program ORFLS (BUSING et al., 1962) was used.

The program permits to assign to each site involved in isomorphous replacements two scattering curves, A and B, and to refine the occupancy factors X with the constraint that  $X(A) + X(B) = 1$ . In particular, the neutral atomic scattering curves (International tables for X-Ray Crystallography, Vol. IV, 1974) of Mg and Fe were given to the octahedral sites M(1), M(2) and M(3) and those of Ca and Na to the M(4) site; an atomic scattering curve of composition 0.5 Si + 0.5 Al was computed for the tetrahedral T(1) site and was kept unchanged during the refinement. For the A site only the scattering curve of Na was used and the occupancy was allowed to vary from 0 to 1 in the course of the refinements. No extinction correction was applied.

In the first stage of the refinements, isotropic temperature factors were used; successively the atoms, all but the hydrogen of the hydroxyl group and Na of the A

TABLE 2  
*Data collection and refinement informations*

	crystal No.2	crystal No.10	crystal No.5
Size of crystal (mm)	0.35x0.18x0.08	0.20x0.15x0.08	0.18x0.16x0.05
Scan width (ω-scan)	2.74	2.4	2.0
Scan speed (°/sec)	0.05	0.06	0.04
No. of non-equivalent $I > 0$	1373	1373	1369
No. of non-equivalent $I > 3\sigma I$	1068	1068	1035
$R_{sym}$ (see text)	0.015	0.016	0.017
Final R (observed data)	0.024	0.024	0.025
Final R (Total)	0.038	0.038	0.040
Cell volume (Å <sup>3</sup> )	903.8	906.0	905.4
Formula unit weight	857.8	862.0	865.1
Calc. density (g/cm <sup>3</sup> )	3.152	3.159	3.173

site, were treated anisotropically. The reflections with  $I > 3\sigma I$  were utilized for the refinements with equal weight. The same sequence of refinement steps was used for the three amphiboles in order to ensure homogeneous and comparable results. The sequence of steps was devised so as to avoid correlations between variables: in each least-squares cycle atomic coordinates and thermal parameters or occupancies or scale factors were allowed to vary.

When the refinement of the atomic parameters of the tetrahedral and octahedral portions of the structures reached convergence, a difference Fourier synthesis was computed: the highest peak in the maps corresponded to the A site. This site appeared in the three samples partially disordered, consistent with previous works on amphiboles (HAWTHORNE and GRUNDY, 1972, 1973 a, b). The maximum of residual electron density was in the A<sub>2</sub> position (coordinates 0,y,0) and lower peaks appeared at the A (0,1/2,0) and A<sub>m</sub> (x,1/2,z) positions. A successive difference Fourier synthesis,

computed including the contributions of the  $A_2$ ,  $A$  and  $A_m$  sites, showed, for the three samples, a strong peak corresponding to the hydrogen atom of the hydroxyl group. This atom was introduced in the last refinement cycle with an isotropic temperature factor equal to that of the oxygen atom bonded to it and with full occupancy. In the difference Fourier maps, the most prominent feature, besides the hydrogen atom, was a peak occurring at about 0.5 Å from M(4) position: the coordinates of this peak correspond to those of the M(4) site in cumingtonite (FISHER, 1966) and grunerite (FINGER and ZOLTAI, 1967) where it is occupied mainly by Fe. A more detailed description of this feature will be given in a further paper. To this second M(4) site, labelled M(4'), was given the atomic scattering factor of Fe; its occupancy was allowed to vary with the constraint that  $M(4) + M(4') = 1$ . Other informations on X-ray data collection and refinement are given in table 2.

Positional and thermal parameters, observed and calculated structure factors and all the structural data which have been omitted for the sake of brevity, are available from the « Istituto di Mineralogia, Università di Pavia, Via Bassi 4, Italy ».

### Crystal chemical results

#### *Tetrahedral sites*

In the tetrahedral chains of amphiboles, replacement of Si by Al can occur. Owing to the small differences in the atomic scattering powers of Al and Si, it is not possible to carry out site occupancy refinements using X-ray data. However the  $Al^{IV}$  content of a tetrahedron can be determined indirectly from T-O bond distances.

In tremolite (PAPIKE et al., 1969) only silicon occupies the center of both T(1) and T(2) tetrahedra and the mean T-O distances are respectively 1.620 and 1.632 Å. When some  $Al^{IV}$  is present, it concentrates in the T(1) site (ROBINSON et al., 1973; HAWTHORNE and GRUNDY, 1973 a, b, 1976).

Table 3 shows that the mean T(1)-O distances of the three examined amphiboles are larger than those of tremolite, and that the mean T(2)-O bond lengths are nearly equal; the slight lengthening which can be observed in the Gorduno amphiboles in respect to tremolite, could be due to the trivalent cations linked to O(2) and O(4), so weakening the T(2)-O(2) and T(2)-O(4) bonds.

On the basis of several refinements of amphiboles, carried out at the « Istituto di Mineralogia » of Pavia (paper in preparation), a good linear relationship (plotted in fig. 2) between T(1)-O mean distances and  $Al/(Al + Si)$  ratio in amphiboles was determined. It can be expressed as:

$$Al^{IV} \text{ (per formula unit)} = (\langle T(1)-O \rangle - 1.620) \times 37.7$$

The  $Al^{IV}$  contents of the three examined amphiboles deduced from the plot of fig. 2 are respectively 38.7 %, 44.3 % and 46.2 %. From these values the anionic parts of the three structures result to be as follows:

TABLE 3  
Tetrahedral bond distances ( $\pm 0.002 \text{ \AA}$ ) compared for three 70-AM-10  
amphiboles and tremolite

	Crystal No.2	Crystal No.10	Crystal No.5	TREMOLITE
T(1) - O(1)	1.651	1.658	1.654	1.602
- O(5)	1.671	1.679	1.675	1.632
- O(6)	1.670	1.678	1.675	1.629
- O(7)	1.653	1.661	1.663	1.616
<T(1) - O>	<u>1.661</u>	<u>1.669</u>	<u>1.667</u>	<u>1.620</u>
T(2) - O(2)	1.632	1.630	1.626	1.616
- O(4)	1.605	1.601	1.596	1.586
- O(5)	1.645	1.645	1.647	1.653
- O(6)	1.656	1.659	1.661	1.672
<T(2) - O>	<u>1.635</u>	<u>1.634</u>	<u>1.633</u>	<u>1.632</u>

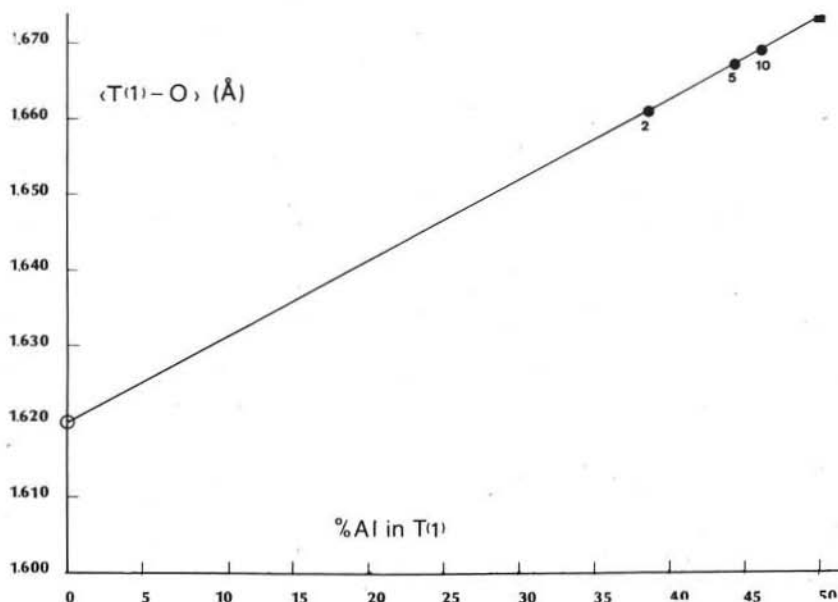


Fig. 2. — A plot of the <T(1)-O> mean distances as a function of atomic percent Al. Circle: tremolite (PAPIKE et al., 1969); square: ferrotschermakite (HAWTHORNE and GRUNDY, 1973; 2 Al<sup>IV</sup> atoms per formula unit from wet chemical analysis).

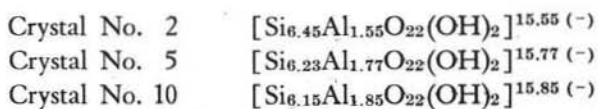


TABLE 4  
Bond distances ( $\text{\AA}$ ) in  $M(1)$ ,  $M(2)$ ,  $M(3)$ ,  $M(4)$  and  $A$  sites

Bond distance	Bond multiplicity	Crystal No.2	Crystal No.10	Crystal No.5
M(1) - O(1)	2	2.051 (1)	2.048 (1)	2.049 (2)
(2)	2	2.115 (2)	2.117 (2)	2.112 (2)
(3)	2	2.096 (1)	2.095 (1)	2.095 (2)
<M(1) - O>		<u>2.087</u>	<u>2.087</u>	<u>2.085</u>
M(2) - O(1)	2	2.064 (2)	2.068 (2)	2.086 (2)
(2)	2	2.047 (1)	2.055 (1)	2.066 (2)
(4)	2	1.959 (2)	1.967 (2)	1.981 (2)
<M(2) - O>		<u>2.023</u>	<u>2.030</u>	<u>2.044</u>
M(3) - O(1)	4	2.093 (1)	2.083 (2)	2.075 (2)
(3)	2	2.073 (2)	2.073 (2)	2.067 (2)
<M(3) - O>		<u>2.086</u>	<u>2.080</u>	<u>2.072</u>
M(4) - O(2)	2	2.393 (2)	2.398 (1)	2.394 (1)
(4)	2	2.303 (2)	2.313 (2)	2.299 (2)
(5)	2	2.659 (2)	2.642 (2)	2.651 (2)
(6)	2	2.581 (2)	2.589 (2)	2.607 (2)
<M(4) - O>		<u>2.484</u>	<u>2.486</u>	<u>2.488</u>
A - O(5)	4	3.030 (3)	3.045 (3)	3.045 (3)
(6)	4	3.086 (4)	3.065 (4)	3.054 (4)
(7)	2	2.436 (3)	2.429 (2)	2.402 (3)
<A - O>		<u>2.934</u>	<u>2.930</u>	<u>2.920</u>
A <sub>2</sub> - O(5)	2	2.714 (2)	2.677 (3)	2.664 (3)
(6)	2	2.833 (3)	2.771 (3)	2.751 (3)
(7)	2	2.467 (2)	2.472 (3)	2.449 (3)
<A <sub>2</sub> - O>		<u>2.671</u>	<u>2.640</u>	<u>2.621</u>
A <sub>m</sub> - O(5)	2	3.083 (3)	3.108 (4)	3.114 (4)
(5')	2	3.072 (3)	3.056 (3)	3.051 (4)
(6)	2	2.718 (3)	2.738 (3)	2.722 (4)
(7)	1	2.348 (3)	2.385 (3)	2.369 (3)
(7')	1	2.634 (3)	2.561 (3)	2.528 (3)
(7'')	1	3.220 (3)	3.293 (3)	3.305 (3)
<A <sub>m</sub> - O> (8 distances)		<u>2.841</u>	<u>2.844</u>	<u>2.834</u>
<A <sub>m</sub> - O> (9 distances)		<u>2.883</u>	<u>2.894</u>	<u>2.886</u>

(e.s.d. in parentheses).

It is observed that the Al<sup>IV</sup> content of the samples No. 5 and No. 10 are essentially the same, coming from mean T(1)-O distances whose differences are very close to the estimated standard deviations.

On the contrary, the Al<sup>IV</sup> content for the crystal No. 2 is significantly different.

#### *A and M(4) sites*

Bond distances for the A and M(4) sites are listed in table 4. The first of the three positions, A, A<sub>2</sub> and A<sub>m</sub>, in which the vacant sites of amphiboles can be



splitted, is occupied only by K and the second only by Na. This distribution is consistent with the observation that the A site (at  $0,1/2,0$ ) has a ten-fold coordination and a mean distance of  $2.93 \text{ \AA}$ , both typical of K. The  $A_2$  site (at  $0,y,0$ ) is six-fold coordinated with a mean bond distance of  $2.65 \text{ \AA}$ : these features are in favour of Na and unsuitable for K. More difficult, in these and in other amphiboles so far investigated, is the crystal chemical characterization of the  $A_m$  site (at  $x,1/2,z$ ); coordinations (8-9 fold) and mean cation-oxygen distances ( $2.83\text{-}2.89 \text{ \AA}$ ) are in fact suitable for both K and Na.

In the present refinements, the  $A_m$  site has been considered occupied by Na in samples 5 and 10 and K in sample 2, on the basis of charge balance requirements (see below).

TABLE 5  
*A and M(4) site populations*

Site	Multiplicity	Crystal No.2	Crystal No.10	Crystal No.5
A	1	0.03 K	0.07 K	0.05 K
$A_2$	2	0.28 Na	0.275 Na	0.315 Na
$A_m$	2	0.035 K	0.095 Na	0.095 Na
Total atoms per formula unit in the A site		$K_{0.10}Na_{0.56}$	$K_{0.07}Na_{0.74}$	$K_{0.05}Na_{0.82}$
M(4)	2	0.91 Ca 0.06 Na	0.95 Ca 0.025 Na	0.92 Ca 0.04 Na
M(4')	2	0.03 Fe	0.025 Fe	0.04 Fe
Total atoms per formula unit in the M(4) site		$Ca_{1.82}Na_{.12}Fe_{.06}$	$Ca_{1.90}Na_{.05}Fe_{.05}$	$Ca_{1.84}Na_{.08}Fe_{.08}$
Sum of the electrostatic charges in the A + M(4) sites		4.54(+)	4.76(+)	4.79(+)

The M(4) site is less questionable: the relative abundance of Ca and Na can be directly determined from the site refinement and Fe tends to concentrate in its own M(4') site.

The occupancy data for A and M(4) sites are summarized in table 5. The sum of the positive charges in the A and M(4) sites is nearly identical in samples 5 and 10, but significantly lower in sample 2. It is easy to observe the relationship existing between these quantities and the amount of tetrahedral Al. This means that the charge balance is ensured by the A + M(4) sites rather than by the octahedral cations. In fact the sums of the charges of the octahedral cations, computed on the basis of the considerations made till now, are the following:

	tetrahedra		A + M(4)		M(1) + M(2) + M(3)
Sample No. 2	15.55	—	4.54	=	11.01
» No. 10	15.85	—	4.76	=	11.09
» No. 5	15.77	—	4.79	=	10.98

TABLE 6

Mean M-O bond distances ( $\text{\AA}$ ) and number of electrons of the octahedral sites calculated from (Fe, Mg) atomic scattering factors

Site	Multiplicity		Crystal No.2	Crystal No.10	Crystal No.5
		Fe	0.166	0.192	0.206
		Mg	0.834	0.808	0.794
M(1)	2	total electrons	14.32	14.69	14.88
		M(1) - O	2.087	2.087	2.085
		Fe	0.173	0.167	0.171
		Mg	0.827	0.833	0.829
M(2)	2	total electrons	14.42	14.34	14.39
		M(2) - O	2.023	2.030	2.044
		Fe	0.270	0.284	0.292
		Mg	0.730	0.716	0.708
M(3)	1	total electrons	15.78	15.98	16.09
		M(3) - O	2.086	2.080	2.072
		total electrons in the M sites	73.26	74.04	74.63
		average M-O bond distances	2.061	2.063	2.066

Mean e.s.d. for occupancy is 0.003.

These values, which are close to one another, can be considered reliable enough, as the main source of errors is the characterization of the  $A_m$  sites, which can be occupied both by K and Na. However, the amounts of atoms involved in the  $A_m$  sites are so small that cannot significantly modify the total charges given above for the octahedral cations. The resultant charges for M(1) + M(2) + M(3) sites clearly indicate that the total amount of trivalent cations occurring in the octahedral portions is very near to one.

This finding, however, must be evidenced in the octahedral bond distances.

#### Octahedral sites

As previously mentioned, two atomic scattering factors (Fe and Mg) have been given to the M(1), M(2) and M(3) sites during the refinements, leaving the possibility of deducing a more suitable site population to the examination of the M-O bond distances (reported in table 4). Atomic proportion in Fe and Mg given by the refinements for the three octahedral sites (see table 6) have to be considered

TABLE 7

*Octahedral site populations and positive electrostatic charges*

Site	Multiplicity	Site population	Crystal No.2	Crystal No.10	Crystal No.5	
M(1)	2	Fe <sup>2+</sup>	0.17	0.19	0.17	
		Mg	0.83	0.81	0.79	
		Fe <sup>3+</sup>	0.00	0.00	0.04	
		positive charges	2.00	2.00	2.04	
M(2)	2	Fe <sup>3+</sup>	0.15	0.15	0.11	0.16
		Al	0.32	0.28	0.25	0.18
		Mg	0.53	0.57	0.58	0.66
		Ti <sup>4+</sup>	==	==	0.06	==
		positive charges	2.47	2.43	2.48	2.34
M(3)	1	Fe <sup>2+</sup>	0.22	0.16	0.08	
		Fe <sup>3+</sup>	0.05	0.12	0.21	
		Mg	0.73	0.72	0.71	
		positive charges	2.05	2.12	2.21	
Total electrostatic(+)charges in the octahedral portion			10.99	10.98	11.08	10.97
Total electrostatic(-)charges of the tetrahedral portion and of the A + M(4) sites			11.01	11.09	10.98	

For the M(2) site of crystal No. 10, two site populations have been calculated; that including Ti was computed by imposing charge neutralization.

therefore only in terms of the number of electrons given by the atomic population present in each octahedral site.

As it can be seen from table 6 the number of electrons in homologous sites of the three samples is almost constant; on the other hand the mean bond lengths show remarkable differences.

In particular it appears that:

- the M(2) site shows, in all three structures, the smallest mean bond distance;
- the mean M(2)-O bond length increases in correspondence with a decrease of the mean M(3)-O distance;
- the mean M(1)-O bond lengths are always larger than the corresponding M(3)-O even if the M(1) sites have lower electron contents;
- going from crystal No. 2 to crystal No. 5 the mean M-O bond lengths tend to become similar.

On the basis of these observations and taking into account that Fe<sup>3+</sup> and Al<sup>IV</sup> have ionic radii smaller than Fe<sup>2+</sup> and Mg, it appears that, in the crystal No. 2, high charge cations are mainly ordered in the M(2) site; on the other hand the

crystal No. 5 has high charge cations in all three sites, with the following site preference  $M(1) < M(3) < M(2)$ .

However, if one would obtain quantitative informations about the site population, it is necessary to make the following two assumptions:

- 1) all the octahedral sites have full occupancy;
- 2)  $Fe^{2+}$  does not order with  $Al^{VI}$ .

The former assumption can be supported by the fact that in none of the refinements so far performed or published the need to consider incomplete an octahedral site has never happened. On the other hand, it is a common experience that the major part of the chemical analyses on amphiboles show that the sum of the Y-group cations tends to be  $> 5.0$  rather than  $< 5.0$ . Moreover, the occurrence of vacancies in the octahedral sites is extremely improbable on the basis of local charge balance requirements.

The latter assumption is more questionable; however it is based on the fact that  $Fe^{2+}$  and  $Al^{VI}$  show, among the isomorphous octahedral cations, the highest differences both in ionic radius and ionic charge. Furthermore it appears reasonable that, if some cation order is observed, it firstly should concern ions with the highest crystal chemical differences.

One can therefore conclude that among the four principal cations ( $Al$ ,  $Fe^{3+}$ ,  $Mg$ ,  $Fe^{2+}$ ) which can occupy an octahedral site, a high probability exists that they are only  $Al$ ,  $Fe^{3+}$ ,  $Mg$  or  $Fe^{3+}$ ,  $Mg$ ,  $Fe^{2+}$ .

To the two assumptions reported above the knowledge of the mean bond length of pure octahedral cations can be added. X-ray crystal structure refinements of 30 blue amphiboles of the glaucophane-riebeckite series (UNGARETTI et al., 1978) have given the following values ( $\text{\AA}$ ) for the mean octahedral bond distances:  $Fe^{2+}-O = 2.125$ ,  $Mg-O = 2.078$ ,  $Fe^{3+}-O = 2.031$ ,  $Al^{VI}-O = 1.929$ .

All the elements are now at hand for solving the following equation system:

$$\begin{aligned} X + Y + Z &= 1 \\ n(1)X + n(2)Y + n(3)Z &= N \\ d(1)X + d(2)Y + d(3)Z &= D \end{aligned}$$

where  $X$ ,  $Y$ ,  $Z$  are the percentages of the three cations which are supposed to occupy an octahedral site;  $N$  is the number of electrons calculated from  $Fe$ ,  $Mg$  proportion given by the refinement and  $D$  is the observed mean bond length for that site;  $n(1)$ ,  $n(2)$ ,  $n(3)$  are the atomic numbers of the atoms which, if present, would give respectively  $d(1)$ ,  $d(2)$ ,  $d(3)$  mean bond distances. The equation system gives just one solution with  $X$ ,  $Y$ ,  $Z$  positive or null.

The reliability of the results which can be obtained in this way depends on the following factors:

- 1) the quality of the crystallographic refinement giving  $N$  and  $D$  values;
- 2) the validity of the assumption that the mean bond lengths used for pure octahedral cations,  $d(1)$ ,  $d(2)$ ,  $d(3)$ , are independent from the crystal chemical features of the rest of the structure;

- 3) the validity of the assumption that  $\text{Fe}^{2+}$  does not order with  $\text{Al}^{\text{VI}}$ ;  
 4) the absence of other octahedral ions like, for instance, Ti and Mn.

It is, however, possible to check the results by comparing the positive charges so obtained for the octahedral sites with the negative charges resulting from the crystal chemical characterization of the tetrahedral portion and the  $\text{A} + \text{M}(4)$  sites.

In table 7 the calculated site populations of the octahedral positions of the three examined amphiboles are listed.

TABLE 8  
*Chemical analyses of the three 70-AM-10 amphiboles deduced from  
 crystallographic refinements*

Atoms per formula unit (24 oxygens)	Crystal No.2	Crystal No.10	Crystal No.5	Oxide	Crystal No.2	Crystal No.10	Crystal No.5
Si	6.45	6.15	6.23	$\text{SiO}_2$	45.24	42.87	43.30
$\text{Al}^{\text{IV}}$	1.55	1.85	1.77				
$\text{Al}^{\text{VI}}$	0.64	0.50	0.36				
Al (tot)	2.19	2.35	2.13	$\text{Al}_2\text{O}_3$	13.03	13.90	12.56
$\text{Fe}^{2+}$	0.62	0.59	0.50	FeO	5.20	4.92	4.16
$\text{Fe}^{3+}$	0.35	0.34	0.61	$\text{Fe}_2\text{O}_3$	3.26	3.15	5.63
Ti	0.00	0.12	0.00	$\text{TiO}_2$	0.00	1.11	0.00
Mg	3.45	3.50	3.61	MgO	16.24	16.37	16.83
Ca	1.82	1.90	1.84	CaO	11.92	12.36	11.94
Na	0.68	0.79	0.90	$\text{Na}_2\text{O}$	2.46	2.84	3.23
K	0.10	0.07	0.05	$\text{K}_2\text{O}$	0.55	0.38	0.27
$\Sigma$	15.66	15.80	15.87				
H	2	2	2	$\text{H}_2\text{O}$	2.10	2.09	2.08
				$\Sigma$	100.00	100.00	100.00

It can be seen that the charge balance is particularly good for crystals No. 2 and No. 5. Slightly less satisfactory is the agreement for the crystal No. 10 whose octahedral portion gives 10.98 charges instead of 11.09 required by the rest of the structure. This inconsistency could be due to the presence of some  $\text{Ti}^{4+}$  in  $\text{M}(2)$ , which is the preferential site for high charge cations, because of the charge imbalance of the oxygen O(4) bonded to it. Ti content can be calculated by imposing the additional condition that  $\text{M}(2)$  site has to give 2.48 positive charges, a value required for reaching neutralization. As no reliable Ti-O bond distance estimation for amphiboles is available the value of 1.991 Å has been obtained by subtracting from  $\text{Fe}^{3+}\text{-O} = 2.031$  the difference between the ionic radii (SHANNON, 1976) of  $\text{Fe}^{3+}$  (0.645 Å) and  $\text{Ti}^{4+}$  (0.605 Å). The following equation system has been therefore solved:

$$\begin{aligned}
 (\text{Fe}^{3+})\text{X} + (\text{Al})\text{Y} + (\text{Mg})\text{Z} + (\text{Ti})\text{W} &= 1 \\
 26\text{X} + 13\text{Y} + 12\text{Z} + 22\text{W} &= 14.34 \\
 2.031\text{X} + 1.929\text{Y} + 2.078\text{Z} + 1.991\text{W} &= 2.030 \\
 3\text{X} + 3\text{Y} + 2\text{Z} + 4\text{W} &= 2.48
 \end{aligned}$$

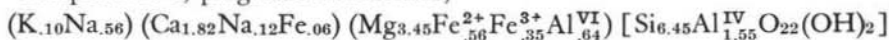
In table 7 the results are compared with those obtained for a three-cation site population.

Ti has been introduced in the site population of the octahedral sites of crystal No. 10 not only to reach a better charge balance, but also to allow for the results of the microprobe analyses which gave 0.02 and 0.09 Ti atoms for the two analyzed amphiboles. Moreover, the crystal No. 10, which is chemically and crystal chemically almost identical to crystal No. 5, is characterized by a brown colour; the hypothesis can be made that the different colour observed for the eclogitic amphiboles from Alpe Arami is due to variation in Ti contents, in analogy with the magmatic hornblendes which are particularly rich in titanium and characterized by a dark brown colour.

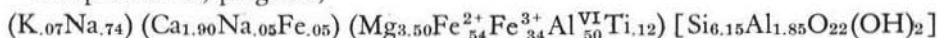
### Conclusions

The three chemical analyses deduced from the crystallographic refinements are listed in table 8. The formula units and names, given according to the nomenclature proposed by I.M.A. Subcommittee on amphiboles (1977), are as follows:

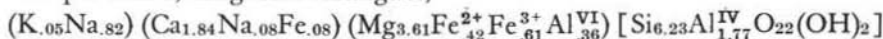
Sample No. 2, pargasitic hornblende,



Sample No. 10, pargasite,



Sample No. 5, magnesio-hastingsite,



However, in present case, it seems more appropriate to consider all the amphiboles from 70-AM-10 eclogite as *pargasites*, being very small the differences in the chemical composition suggesting the different names; furthermore the sample No. 10 (pargasite) is very close to the mean crystal chemical composition of the amphiboles of the host eclogite. In fig. 1 the crystal No. 10 has, in fact, quite the same position of the point calculated from the cell parameters determined with the powder method.

On the basis of the results of the refinements it is now possible to relate, at least qualitatively, the cell parameters to the crystal chemical composition. The position of the sample No. 2 in fig. 1 can be explained on the basis of the minor contents in  $(Na + K)$  of the A site and in  $Al^{IV}$ ; this is in agreement with the close positions of the samples No. 10 and No. 5, which are characterized by very similar  $(Na + K)_A$  and  $Al^{IV}$  contents. It can be therefore concluded that the increase in  $(Na + K)_A$  and in  $Al^{IV}$  is mainly reflected by an increase of the  $a$  cell parameter.

Finally the variation of the  $c \sin \beta / b$  ratio can be related to the  $Al^{VI}$  content, which progressively decreases in the samples No. 2, 10 and 5. However  $c \sin \beta / b$  does not change very much because the  $Al^{VI}$  decrease is compensated by a nearly

identical increase in ( $\text{Fe}^{3+}$ , Ti). This isomorphous replacement has the smallest influence on the geometry of the octahedral portion.

The chemical differences shown by the three refined samples do not cover entirely the range of composition determined in the amphiboles of the 70-AM-10 eclogite by electron microprobe analyses. In the previously mentioned paper (Bocchio, 1977) microprobe analyses of the two amphiboles of the same eclogite, have given a much wider range, particularly in Si,  $\text{Al}^{\text{IV}}$ ,  $\text{Al}^{\text{VI}}$  and Mg contents; from these findings and from petrographic and petrogenetical evidences the two amphiboles were considered of primary and secondary origin.

TABLE 9

*Ranges in cation proportions for eclogitic amphiboles from Alpe Arami*

	I	II	III
Si	6.05 - 6.65	6.15 - 6.45	6.27 - 6.42
$\text{Al}^{\text{IV}}$	1.35 - 1.95	1.55 - 1.85	1.58 - 1.73
$\text{Al}^{\text{VI}}$	0.46 - 0.99	0.36 - 0.64	0.84 - 0.92
Fe (tot)	0.86 - 1.39	0.93 - 1.11	0.96 - 1.02
Ti	0.01 - 0.11	0.00 - 0.12	0.03 - 0.04
Mg	2.85 - 3.72	3.45 - 3.61	3.40 - 3.53
Ca	1.48 - 1.83	1.82 - 1.90	1.28 - 1.38
Na	0.66 - 0.99	0.68 - 0.90	1.18 - 1.27
K	0.00 - 0.13	0.05 - 0.10	0.08 - 0.10

I: microprobe analyses of six amphiboles from five eclogites (ERNST, 1977); II: crystallographic refinements of three amphiboles from 70-AM-10 eclogite; III: microprobe analyses of four close points within a single grain of amphibole from 70-AM-10 eclogite.

New microprobe determinations performed at the « Istituto di Mineralogia e Petrologia » of Modena, confirmed that the chemical variations previously pointed out between the two phases of amphibole may be detected also within a single amphibole grain (table 9).

In addition a chemical composition close to that attributed to the primary amphibole (determined by W.L. GRIFFIN, Oslo, by microprobe analysis on an unaltered and idiomorphic crystal, Bocchio, 1977) has been again found in a prismatic and bladed crystal which, although partially corroded and with inclusions of quartz, plagioclase and rutile, shows petrographic features of a primary origin. However, in the more altered portions of the same crystal and along its cracks some points

with chemical composition intermediate between garnet and omphacite were detected.

This result suggests that the textural equilibrium observed in the primary assemblage is, in particular cases, metastable and that the composition of the early amphibole could be biased by patches of uncomplete reaction between omphacite and garnet determining an anomalous chemical environment.

ERNST (1977) has analyzed with electron microprobe six amphiboles from five eclogitic rocks from Alpe Arami; he obtained a wide range in chemical composition and concluded (pg. 384): «... the amphiboles display seemingly random variations and systematic chemical differences as a function of occurrence remain obscure...».

In table 9 are reported the ranges in cation proportions for amphiboles of five eclogites from Alpe Arami (ERNST' result, 1977), for three amphibole crystals (crystallographic refinement results) and for four different points (core) of a single grain from 70-AM-10 eclogite.

Even neglecting the «alumino ferroanpargasite» (BOCCHIO, 1977) for its uncommon composition and for its possible crystallization before the retrograded symplectite-amphibolite phase, it is clear, from table 9, that all the amphiboles are pargasitic terms, but they show wide chemical variations indicating conditions of disequilibrium. This is additionally confirmed by the crystal chemical differences emerged from the crystallographic refinements.

The most evident crystal chemical feature shown by the three samples analyzed with crystallographic techniques is the partial disorder of the high charge cations over the octahedral sites M(1), M(2) and M(3).

However, cation disorder in amphiboles is not very common. On the basis of more than 50 amphibole structures so far refined at the «Istituto di Mineralogia» of Pavia (unpublished data), only a few of them appear to be characterized by a significant disorder of high charge cations over the three octahedral site. Furthermore the major part of these few disordered amphiboles are volcanic hornblendes. One could therefore suggest that if the temperature of formation is low, as for the glaucophane series, or if the temperature is high but decreases slowly, the structure can reach a perfect order of the smallest ions (Al,  $Fe^{3+}$ , Ti) on the M(2) site. When, on the contrary, the temperature is high but decreases abruptly (as it happens for volcanic hornblendes) the cation disorder remains frozen.

In conclusion the pargasitic amphiboles from Alpe Arami appear to be crystallized at relatively high temperature, in agreement with their  $Al^{IV}$  contents (KOSYUK and SOBOLEV, 1969), which range between 1.55 and 1.85 atoms per formula unit. The chemical variations among different crystals and among different zones of the same crystal seem to indicate that homogeneization was prevented, most probably due to fast cooling rates; this hypothesis is supported by the partial cation disorder observed.

The crystallization appears to be occurred at almost isobaric conditions, being quite constant the high charge cation contents in the analyzed crystals (1 atom



per formula unit). This value suggests pressure of formation intermediate between that relative to tremolites (no high charge cations) and that relative to glaucophanes or tschermakites (2 high charge atoms).

These considerations support the second hypothesis made by ERNST (1977) about the conversion of the Alpe Arami eclogites to amphibolites: «...the eclogites were emplaced in the Lepontine terrane before termination of the relatively high-grade Late Alpine metamorphic event, which subsequently caused the partial replacement of garnet + omphacite assemblage by amphibolite». P, T conditions proposed by ERNST in this case (6-7 kbars and 600-700° C) are in agreement with the crystal chemical features shown by the three amphiboles analyzed with crystallographic techniques.

On the contrary the first hypothesis made by ERNST (P, T conditions of 20 kbars and 800-900° C) would require much higher (Al<sup>vi</sup>, Fe<sup>3+</sup>, Ti) and Al<sup>iv</sup> contents. Additionally these higher temperature conditions (800-900° C) are in conflict with the results obtained by the crystallographic refinement (ROSSI et al., 1978) of the omphacite belonging to the primary assemblage of the 70-AM-10 eclogite.

The examined pyroxene, showing P2/n space group symmetry, is characterized by the maximum possible order both of the octahedral cations and of Ca and Na atoms. This finding implies that the temperature, taking into account the fast cooling rate during conversion of the eclogite to amphibolite, could not have exceeded 725° C (FLEET et al., 1978).

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