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# MINERAL CHEMISTRY OF MAFIC AND ULTRAMAFIC AMPHIBOLITES FROM NORTH-EASTERN SARDINIA

Abstract — Mafic and ultramafic amphibolites, derived from primitive granulitic rocks, outcrop in North-Eastern Sardinia, within migmatites of the K-feldspar + Sillimanite zone.

The results of a systematic electron-microprobe study, performed on 20 amphibolites and 2 migmatites, for a total of about 80 mineral analyses are presented.

The primary paragenesis of ultramafic rocks was Ol+Opx+Grt+Cpx and the distribution of Mg/Fe among these minerals appears as follows: Cpx > Opx > Ol > Grt.

Hbl is the main product mineral of the amphibolite-facies metamorphism and the Mg/Fe partition between this mineral and some relict phases is relatively systematic. Hbl concentrates iron relative to Cpx (KD <sup>Cpx-Hbl</sup> = 1.53) and Mg relative to Opx, Ol, and Grt (KD = 0.76; 0.51; 0.196-0.27 respectively); among amphibolite-facies minerals iron is concentrated in Spl relative to Hbl and Chl (KD<sup>Spl-Hbl</sup> = 0.22; KD<sup>Chl-Hbl</sup> = 1.37).

The large compositional variations shown by Hbl cannot be explained by variations of P-T parameters, but appear controlled both by the composition of the system (nature and proportion of reactant phases) and by the equilibria with coexisting phases (Chl and Spl or Pl).

**Riassunto** — *Mineralogia di anfiboliti femiche e ultrafemiche della Sardegna nord-orientale.* Nel basamento della Sardegna nord-orientale, comprese nelle migmatiti listate della zona a K-feldspato + Sillimanite, affiorano rocce anfibolitiche femiche ed ultrafemiche, derivate da primitive rocce granulitiche.

In questo articolo vengono presentati i risultati di uno studio sistematico, effettuato mediante Microsonda elettronica su 20 anfiboliti e su 2 migmatiti, per un totale di circa 80 analisi di minerali.

La paragenesi primitiva delle rocce ultrafemiche era Ol+Opx+Grt+Cpx e la distribuzione di Mg/Fe fra questi minerali è attualmente la seguente: Cpx > Opx > Ol > Grt.

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#### MEMMI I.

L'orneblenda è il principale minerale formato durante il metamorfismo in facies anfibolitica e la distribuzione di Mg/Fe tra questa e alcune fasi relitte è relativamente sistematica. Hbl concentra Fe rispetto a Cpx ( $KD^{Cpx-Hbl} = 1.53$ ) e Mg relativamente a Opx, Ol e Grt (KD = 0.76; 0.51; 0.196-0.27 rispettivamente), mentre fra i minerali della facies anfibolitica, Fe si concentra in Spl relativamente a Hbl e Chl ( $KD^{Spl-Hbl} = 0.22$ ;  $KD^{Chl-Hbl} = 1.37$ ).

Le variazioni composizionali che si osservano in Hbl non possono essere spiegate mediante variazioni dei parametri fisici P e T, ma sembrano essere controllate sia dalla composizione del sistema (natura e proporzioni delle fasi reagenti) sia dagli equilibri con fasi coesistenti (Chl e Spl o Pl).

Key words — Mafic and ultramafic amphibolites, Microprobe analyses, Mineral chemistry, Element partitioning, North-Eastern Sardinia.

#### INTRODUCTION

Mafic and ultramafic amphibolites, carrying relics of a previous granulitic assemblage, outcrop in Northeastern Sardinia, within migmatites of the K-feldspar+Sillimanite zone (FRANCESCHELLI et al., 1982). In these rocks a complex retrograde evolution of a primary anhydrous granulite-facies assemblage to an amphibolitefacies assemblage has been recognized.

In some previous papers GHEZZO et al. (1979, 1980, 1982) described the petrography of the rocks, analysed the paragenetic compatibilities, estimated the P-T regime operating during the various petrogenetic events and discussed the geologic significance of the granulitic event, in the frame of the Hercynian orogenesis of the Corsican-Sardinian block.

The main petrologic problem that still remains to be solved regards the precise definition and mechanism of the reactions which operated over the different granulitic parageneses during the amphibolite-facies retrogressive event and that produced large amount of amphibole.

To this purpose and for a better understanding of the intraand intercrystalline elemental partition, a combined electronmicroprobe and X-ray diffraction study on both the (granulitefacies) mineral reactants and the (amphibolite-facies) mineral products, was started with the collaboration of the «Centro di Cristallografia Strutturale del CNR» of Pavia (manuscript in preparation).

In this paper, after a brief outline of the geo-petrologic con-

text, we report the results of a systematic electron-microprobe study carried out on all the phases present in twenty amphibolites and two migmatites and discuss some crystal-chemical features.

#### GEO-PETROGRAPHIC OUTLINES

The mafic and ultramafic amphibolites studied in this paper outcrop at M.giu Nieddu,  $\sim$  7 Km North-East of Olbia, and they are part of one of the numerous «roof pendents» of high-grade metamorphites lying on the Hercynian monzogranites and leucogranites (GHEZZO et al., 1979; DI SIMPLICIO et al., 1974).

The metabasites are enclosed within stromatic migmatites with leucosomes either concordant or discordant in respect to the metamorphic foliation.



Fig. 1 - Schematic geologic map of M.giu Nieddu (north-eastern Sardinia). 1 - Quaternary deposits; 2 - Massive ultramafic amphibolites; 3 - Banded plagioclase amphibolites; 4 - Biotite-muscovite paragneisses and migmatites; 5 -  $D_2$  fold axes; 6 -  $S_2$  axial plane scistosity; specimens location is also shown.

a - Post-Hercynian deposits; b - Hercynian granitoids; c - metamorphic basement.

The mafic massif strikes  $\sim$  NS and shows a lenticular shape; it is about 1000 m long and 20-30 m thick. Ultramafic amphibolites and banded plagioclase amphibolites have been recognized within this body (see fig. 1).

The metabasites, and the enclosing migmatites appear to be affected, at mesoscopic scale, by a main tectono-metamorphic phase which produced isoclinal folds (the axes strike N 130 to E-W), flow schistosity and metamorphism ( $M_2$ ) superimposed on rocks having a pre-existing metamorphic foliation ( $S_1$ ) (see FRANCESCHELLI et al., 1982).

On normative basis, the rocks of the M.giu Nieddu massif show a composition ranging from olivine mela-gabbros, quartzgabbros, leuco-gabbros to trondhjemites (GHEZZO et al., 1979).

A petrochemical affinity between mafic and ultramafic rocks, which are probably genetically related by processes of cumulitic differentiation of an original continental rift type tholeiitic basaltic magma, has been suggested (GHEZZO et al., 1979; МЕММІ et al., 1982).

### Massive ultramafic amphibolites (U.A.)

These rocks, in spite of a normative content of feldspar higher than 20%, have an ultramafic modal composition.

Mineral assemblages (see table 1) consist of Hbl  $\pm$  Ol  $\pm$  Grt  $\pm$  Opx  $\pm$  Cpx  $\pm$  Chl  $\pm$  Spl (<sup>1</sup>).

Textural evidences indicate that a pre-existing anhydrous paragenesis was deeply converted to a typical amphibolite-facies paragenesis. The primary minerals, that normally represent less than 50% of the assemblages, are Grt, Ol, Opx, Cpx.

These minerals occur as relics with irregular margins, rounded and lobated, generally enclosed within the Hbl; they never occur all together in the same sample and, with the exception of Ol-Opx pair, are never in contact with one another.

Cpx (rare relics in few samples) does not occur in rock containing Opx.

The minerals developed during the successive amphibolitefacies metamorphism are predominantly calcic amphiboles and subordinately green spinel and chlorite.

<sup>(1)</sup> In this paper the symbols proposed by KRETZ (1983) are used both for minerals (capital case) and components (lower case).

Opaque minerals are rare and are represented by magnetite with subordinate ilmenite lamellae, occasionally ematite and, more rarely, pyrrhotite.

Sample	Grt	01	Opx	Cpx	Hbl	Pl	Spl	Chl	Ath	Qtz	Ep	Ap	Spn	Fe-Ti	Ox
566					x			x	x					tr	
556	tr	х			х		х	x						tr	
555		х		tr	х		x	х						×	
551		х			х		x	х						tr	
572		х		tr	х		x	x						×	
310	х	x	х		х		x							tr	
553	х	х	х		х		x							tr	
548	х	х	х		х		x							tr	
550			х		х		x	tr						tr	
549	x			tr	х		x	tr			tr			tr	
311C	х				х	tr					tr	tr			
311B	x				х	x				x	tr			tr	
552	х				х	x		tr			x			tr	
545				x	х	х							x	tr	
306					х	х				x		tr	x	x	
305	x				х	х				x	tr	tr		x	
308					х	х					tr		tr	tr	
311A	x				х	х				х	tr			tr	
546					х	х		tr			tr		tr	tr	
1236					х	х					x		x	tr	

 TABLE 1 - Visual estimation of modal composition of ultramafic and plagioclase amphibolites.

tr < 1%, x 1-10%, X > 10%

# Banded plagioclase amphibolites (P.A.)

These rocks consist of Hbl + Pl (in apparent textural equilibrium)  $\pm$  Grt  $\pm$  Cpx  $\pm$  Qtz.

Garnet, abundant in same samples, has a poekiloblastic character; it is often deformed and shows rounded and lobated margins in relation to the incipient reaction with Hbl and Pl.

Cpx is rare; it occurs in poligonal association with Hbl and Pl and shows evidence of instability in respect to Hbl.

Epidote is sometime abundant as in sample no. 1236. Opaque minerals are very rare; some samples carry sphene.

# Gneisses and migmatites (M.)

Within the surrounding para-metamorphites, the mineral assemblages consist of  $Qtz+Pl+Bio+Ms+Grt\pm Kfs$  with, at place, Ky and/or Sil.

In these rocks the evidence of microtextural disequilibrium is limited to: instability of kyanite, late intergranular development of fibrolitic sillimanite, appearance of garnet and its Mn reverse zoning (see below).

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According to GHEZZO et al. (1979, 1982) the P-T conditions, estimated on the basis of well known experimental equilibria (see fig. 7 in GHEZZO et al., 1979), were  $\sim$  750° C,  $\sim$  10 Kb and P<sub>H2O</sub> << P<sub>s</sub> for the granulitic event and  $\sim$  650° C,  $\sim$  5 Kb and P<sub>H2O</sub> = P<sub>s</sub> for the amphibolitic one.

The later should be related to the second Hercynian tectonometamorphic phase (FERRARA et al., 1978), whereas, for the former, eo-Hercynian to older ages have been proposed (GHEZZO et al., 1979, 1982).

#### MINERAL CHEMISTRY

#### Methodology

All the minerals of 22 samples (10 ultramafic, 10 plagioclase amphibolites and 2 migmatites) were microprobe analysed, with an ARL-SEMQ instrument, operated in the wavelength dispersive mode, at 15 Kv, 20  $\mu$ A beam-current.

On line data reduction was based on the ZIEBOLD and OGILVIE (1964) method, by the use of ALBEE and RAY (1977) correction factors.

Natural albite, microcline, olivine, clinopyroxene, garnet, amphibole and chromite were used as standards.

The minerals are generally unzoned and of quite uniform composition (with few exceptions), in the domain represented by the thin section. Therefore, each analysis reported in tables 2-9 represents the average of 5-15 spots, performed on different grains of the same thin section.

ABLE 2	۰.	Microprobe	analyses	and	structural	formulae	of	garnets	from	ultramafic
ana	d 1	plagtoclase a	amphibolity	es an	d migmati	tes.				

	U.A.					P.A.					м.		
Sample	556	310	553	548	549	311C	311B	552	305	311A	543rim	543core	568
si0,	39.86	38.59	39.16	39.14	39.24	38.83	38.15	38.52	38.27	37.83	36.64	36.86	36.81
ALOGA	23.33	22.18	21.95	23.21	22.31	22.28	21.90	21.44	21.82	21.73	21.81	21.19	21.96
TIO,	0.00	0.02	0.00	0.00	0.00	0.00	0.02	0.06	0.03	0.00	0.00	0.00	0.00
FeO	20.59	21.76	22.14	21.68	20.61	26.58	26.77	26.00	.28.42	29.65	30.70	32.26	30.29
CL 202	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mno	1.62	0.77	0.96	1.11	1.24	1.39	1.26	0.68	1.79	1.03	6.71	4.12	7.53
OpM	. 10.92	10.91	9.58	10.00	6.80	8.24	7.25	5.38	4.82	4.17	2.34	3.21	3.07
CaO	5.25	5.33	6.33	5.61	10.87	4.14	5.08	8.41	6.49	6.67	1.38	1.30	1.17
Tot	101.57	99.56	100.12	100.75	101.07	101.46	100.43	100.49	101.64	101.08	99.58	98.94	100.83
Formula	basis 12 c	. suaptions											
Si	2.963	2.945	2.984	2.949	2.981	2.965	2.959	2.995	2.971	2.965	2.968	2.993	2.946
ALIV	0.037	0.055	0.016	0.051	0.019	0.035	0.041	0.005	0.029	0.035	0.032	0.007	0.054
ALVI	2.007	1.940	1.955	2.009	1.978	1.970	1.960	1.959	1.968	1.973	2.050	2.020	2.016
Ti	0.000	0.001	0.000	0.000	0.000	0.000	0.001	0.004	0.002	0.000	0.000	0.000	0.000
Fe	1.280	1.389	1.410	1.366	1.309	1.697	1.736	1.690	1.845	1.943	2.079	2.190	2.026
Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mn	0.102	0.050	0.062	0.071	0.080	060.0	0.083	0.045	0.118	0.068	0.460	0.283	0.510
Mg	1.209	1.240	1.087	1.122	0.769	0.937	0.838	0.623	0.557	0.487	0.282	0.388	0.366
Ca	0.418	0.436	0.517	0.453	0.884	0.339	0.422	0.700	0.540	0.560	0.120	0.113	0.100
Sum	8.015	8.056	8.031	8.021	8.020	8.032	8.039	8.020	8.029	8.031	7.991	7.994	8.019
alm	42.53	44.58	45.85	45.35	43.02	55.41	56.39	55.26	60.30	63.53	70.68	73.62	67.48
sds	3.39	1.60	2.01	2.35	2.62	2.93	2.69	1.46	3.85	2.24	15.65	9.52	16.99
prp	40.19	39.83	35.35	37.27	25.29	30.60	27.21	20.37	18.22	15.92	9.60	13.05	12.19
grs	13.89	13.99	16.79	15.03	29.07	11.06	13.71	22.90	17.64	18.31	4.07	3.80	3.34
Ma/Fe"	0.945	0.893	0.771	0.822	0.588	0.552	0.483	0.369	0.302	0.251	0.136	0.177	0.181

In some cases, when the differences among the spot analyses were higher than the presumed analytical error, and when either zoning (f.i. Grt 543) or non uniform chemical composition (f.i. Opx 550; Spl 556; Hbl 549) were evident, individual spot-analyses are also reported.

For all the minerals, except spinels and amphiboles, iron was assumed to be present in the divalent state.

For spinels the amount of Fe<sup>3+</sup> has been estimated from stoichiometric considerations (see below).

For amphiboles, because of the importance of the oxidation ratio in the calculation of the structural formulae, the divalent iron was determined, by titration with KMnO<sub>4</sub> on nine concentrates ( $\sim$  98% pure) obtained by Franz magnetic separator, heavy liquids and hand picking. The measured Fe<sup>2+</sup>/Fe<sub>tot</sub> ratio ranges from 0.74 to 0.85 and the mean value of 0.81 has been attributed to the other samples.

### Garnet

Ten analyses of garnets of ultramafic and plagioclase amphibolites are presented in table 2, together with three analyses of garnets of migmatites (core and rim composition of sample 543 have been reported).

Total cation contents, based on 12 oxygens, range from 7.99 to 8.05 atoms per formula unit (hereafter at.p.f.u.).

The Si contents (2.94-3.00 at.p.f.u.) appear to be very close to the ideal value of 3.00. The small amounts of  $Al^{IV}$  reported in the table are considered essentially due to analytical errors.

Al<sup>v1</sup> values, which closely approach the ideal value of 2.00 (1.94-2.05 at.p.f.u.) indicate that no significant amounts of Fe<sup>3+</sup> are actually present in the garnets.

Alkalies and chromium are absent in these minerals. The Ti content is also very low.

The composition of garnet may therefore be shown as proportion of Mg, Fe, Ca, Al and Mn as in fig 2a-2b and fig. 3a-3b. The garnets of the ultramafic amphibolites show a rather constant alm content ( $\sim$  44%), and some variations of the prp/grs ratio. The garnets of the plagioclase amphibolites have a higher alm and grs contents.

The garnets of the two analysed migmatites appear to be ve-



Fig. 2 - Mg-Fe-(Ca+Mn) and Ca-Mn-(Mg+Fe) plots for garnet. Tie-line joins core (c) and rim of garnet no. 543. Filled circles = ultramafic amphibolites; open circles = plagioclase amphibolites; open squares = migmatites.



Fig. 3 - Ca-Mg-Fe(a) and Al-Mg-Fe(b) plots for garnet, olivine, orthopyroxene, clinopyroxene and hornblende. In fig. 3b tie-lines join coexisting pairs of minerals (same symbols as fig. 2).

ry different. In rock no. 568, the garnets never are larger than 100 microns and show a nearly homogeneous composition closed to a spessartine-rich almandine.

In rock no. 543, the garnets are larger than 500 microns and have a strongly manganese-rich rim, very similar in composition to that of garnet 568, whereas the core is a typical almandine. Fig. 4 illustrates the chemical variations along a rim-core-rim traverse across a garnet-crystal 940  $\mu$ m long, in sample no. 543.





### Olivine

Seven analyses of olivines are presented in table 7.

Total cation contents (5.99-6.03 at.p.f.u.), calculated on the basis of 8 oxygens, very closely approach the ideal value of 6.

 
 TABLE 3 - Microprobe analyses and structural formulae of olivines from ultramafic amphibolites.

Sample	556	555	551	572	310	553	548
SiO2	37.56	36.66	37.05	37.76	36.82	37.21	37.03
Al203	0.31	0.00	0.00	0.00	0.00	0.00	0.00
TiO2	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FeO	25.28	27.66	29.51	29.19	27.32	28.10	27.68
MnO	0.32	0.46	0.46	0.68	0.16	0.21	0.38
MgO	35.67	34.22	32.79	33.31	33.86	34.62	35.40
CaO	0.02	0.00	0.02	0.00	0.00	0.00	0.00
Tot	99.16	99.00	99.83	100.94	98.16	100.14	100.49
Formula b	asis 8 oxyg	ens					
Si	2.000	1.984	2.002	2.012	2.003	1.989	1.972
Al	0.019	0.000	0.000	0.000	0.000	0.000	0.000
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe	1.125	1.252	1.333	1.301	1.243	1.256	1.232
Mn	0.014	0.021	0.021	0.031	0.007	0.010	0.017
Mg	2.829	2.759	2.640	2.644	2.744	2.757	2.808
Ca	0.001	0.000	0.001	0.000	0.000	0.000	0.000
Sum	5.990	6.016	5.998	5.988	5.997	6.011	6.028
Mq/Fe"	2.51	2.20	1,98	2.03	2.21	2.20	2.28

 
 TABLE 4 - Microprobe analyses and structural formulae of orthopyroxenes and clinopyroxenes from ultramafic and plagioclase amphibolites.

	U.A.							_	P.A.
			Opx				Cp	x	
Sample	310	553	548	550a	550b	555	572	549	545
SiO2	53.60	53.76	53.11	52.82	54.29	52.68	53.40	53.30	50.73
A1203	1.95	1.46	1.83	2.86	1.24	1.06	1.29	1.08	0.98
TiO2	0.01	0.00	0.00	0.01	0.02	0.07	0.08	0.11	0.07
FeO	16.36	16.74	16.86	16.19	15.40	4.12	4.62	5.28	8.06
Cr203	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.01	0.00
MnO	0.18	0.20	0.23	0.14	0.22	0.11	0.21	0.14	0.27
MgO	28.26	27.57	27.44	27.68	28.63	16.60	16.30	15.86	14.19
CaO	0.24	0.23	0.22	0.15	0.16	24.28	23.40	22.79	23.93
Na <sub>2</sub> O	0.00	0.00	0.00	0.00	0.00	0.04	0.04	0.17	0.28
Tot	100.60	99.96	99.69	99.85	99.96 '	98.96	99.41	98.74	98.51
Formula	basis 6 ox	ygens							
Si Al <sup>IV</sup>	1.928 0.072	1.948	1.933	1.912 0.088	1.954	1.955 0.045	1.969 0.031	1.981 0.019	1.935 0.044
AlVI	0.010	0.010	0.011	0.034	0.007	0.002	0.025	0.029	0.000
Ti	0.000	0.000	0.000	0.000	0.001	0.002	0.002	0.003	0.002
Fe	0.492	0.507	0.513	0.490	0.463	0.128	0.142	0.164	0.257
Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000
Mn	0.005	0.006	0.007	0.004	0.007	0.003	0.007	0.004	0.009
Mg	1.514	1.488	1.488	1.492	1.535	0.918	0.895	0.878	0.806
Ca	0.009	0.009	0.009	0.006	0.006	0.965	0.924	0.907	0.978
Na	0.000	0.000	0.000	0.000	0.000	0.003	0.003	0.012	0.021
Sum	4.031	4.021	4.028	4.027	4.019	4.021	4.001	3.998	4.051
Mg/Fe"	3.08	2.93	2.90	3.05	3.31	7.18	6.29	5.35	3.14

Silicon contents (1.97-2.01 at.p.f.u.) are closed to the ideal value of 2.0. Olivine no. 556 apparently carries minor Al.

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All the samples have low but significant amounts of Mn (0.01-0.03 at.p.f.u.).

The composition ranges from fo<sub>66</sub> to fo<sub>72</sub> (see fig. 3a).

### Orthopyroxene

Analyses of five orthopyroxenes are presented in table 4.

The sum of cations per six oxygens tends to be systematically higher (4.02-4.03) than the ideal value of 4.

The silicon contents range from 1.91 to 1.95 at.p.f.u., indicating small but significant Al<sup>IV</sup> substitution.

The total Al content is low (see fig. 3b) and mainly in the four-fold coordination. The Ca content is very low (0.006-0.009 at.p.f.u., fig. 3a) and the overall compositions show little scatter around  $en_{74}$  fs<sub>25</sub> wo<sub>1</sub>.

Two slightly different orthopyroxenes occur in rock no. 550; the composition marked with a in table 4 refers to Opx which is in contact with spinel and is characterized by a lower Si, higher Al and a slightly lower Mg/Fe ratio than that not in contact with spinel.

### Clinopyroxene

Analyses of four clinopyroxenes (three from ultramafic and one from plagioclase amphibolites) are presented in table 4.

The sum of cations, based on 6 oxygens (4.00-4.05 at.p.f.u.), is close to the ideal value of 4.

The silicon proportions range from 1.94 to 1.98 at.p.f.u. The Al content is very low (see fig. 3b) and apparently in the four-fold coordination.

The sodium contents are almost negligible in two samples, whereas a slightly higher content was found in samples nos. 549 and 545 (0.012 and 0.021 at.p.f.u., respectively).

Ignoring the minor en + fs solid solution and the very minor jd content of samples nos. 549 and 545, the composition of clinopyroxenes from the ultramafic rocks ranges from  $di_{88}$   $hd_{12}$  to  $di_{85}$   $hd_{15}$ , and that from the plagioclase amphibolite is  $di_{75}$   $hd_{25}$ . TABLE 5 - Microprobe analyses and structural formulae of amphiboles from ultramafic and plagioclase amphibolites.

42.01 0.49 3.08 9.29 0.00 0.11 11.14 112.43 1.96 0.15 98.18 0.000 0.000 1.926 0.074 5.496 6.078 1.066 0.000 0.053 0.335 2.401 1.124 1.124 0.013 4.992 2.000 0.028 0.503 549c 0.476 2.14 50.79 6.58 0.25 6.45 6.45 0.06 0.15 0.15 17718 12.50 0.78 0.08 96.96 0.007 0.027 0.229 3.647 0.000 0.023 0.018 1.908 0.015 7.239 0.344 0.746 5.000 0.051 2.000 0.164 0.179 15.179 549b 4.74 44.58 11.65 0.52 2.78 8.39 8.39 0.00 0.15 11.78 1.80 0.18 1.836 97.09 0.487 0.000 0.057 0.304 3.309 0.843 0.843 5.000 0.000 0.178 0.018 0.000 2.033 6.489 0.508 0.541 15.574 0.77 549a 3.24 45.09 11.51 0.27 1.96 7.51 7.51 0.10 0.10 0.10 2.10 2.10 2.10 96.64 6.532 0.497 0.000 0.029 0.214 3.716 0.544 0.544 5.000 0.000 0.366 0.012 1.660 0.000 2.038 0.589 0.623 5.661 4.08 1 550 46.67 11.32 0.14 1.94 7.45 0.09 0.10 11.64 96.77 6.715 0.635 0.010 0.015 0.210 3.536 0.694 0.000 5.000 0.000 0.202 0.012 1.794 1.34 0.000 2.008 0.009 0.383 0.374 5.391 1 3.83 548 45.84 11.04 0.17 1.89 7.23 0.00 0.00 12.04 96.01 0.000 0.019 0.207 3.517 0.702 0.702 5.000 0.000 0.176 1.875 0.000 1.51 6.664 0.555 2.051 0.425 0.435 5.486 ULTRAMAFIC AMPHIBOLITES 1 4.01 553 45.77 11.49 0.17 1.86 7.15 0.00 0.00 0.02 116.66 0.00 96.96 6.593 0.543 0.000 0.018 0.202 3.575 0.662 0.662 5.000 0.000 0.199 0.000 15.533 1.891 2.092 0.000 0.441 0.441 1 4.15 310 9.47 9.47 0.17 1.78 6.84 6.84 6.84 0.17 0.17 16.20 112.46 0.81 0.81 0.08 96.33 0.015 0.193 3.472 0.756 0.000 5.000 0.000 0.066 0.021 1.920 0.000 0.240 6.956 0.561 0.000 2.007 0.226 15.247 4.22 I 572 46.72 10.34 1.82 7.00 0.12 7.00 0.12 115.89 11.34 1.34 0.04 95.33 6.812 1.188 0.589 0.000 0.027 0.200 3.451 0.733 0.000 5.000 0.000 0.120 0.015 1.844 2.000 0.358 0.021 0.365 15.365 0.007 4.05 1 551 9.64 9.64 0.23 1.30 6.63 6.63 6.63 0.06 0.07 17.30 12.82 1.04 1.04 0.08 96.53 6.816 0.451 0.007 0.141 3.709 0.667 0.000 5.000 0.000 0.130 0.009 1.976 0.000 2.115 0.290 0.015 0.305 15.420 0.85 4.65 555 48.89 0.18 0.18 1.52 5.82 0.10 0.11 0.11 96.93 0.616 0.019 0.162 3.629 0.563 0.000 5.000 0.000 0.128 1.809 0.050 1.15 6.940 0.011 2.000 0.267 0.014 0.281 15.281 5.25 1 556 57.70 0.56 0.00 0.00 13.33 0.00 0.27 0.27 0.43 8.014 0.000 0.000 0.000 4.908 0.000 0.000 1.548 0.032 0.08 97.41 0.092 5.000 0.272 0.064 1.937 0.000 0.000 0.000 14.951 0.022 566b 3.35 1 Formula basis 23 oxygens 45.75 11.40 0.51 1.80 6.91 6.91 6.91 0.09 0.08 11.73 11.73 1.92 0.19 6.657 0.010 95.90 0.612 0.056 0.197 3.364 0.761 0.000 5.000 0.000 0.080 0.010 1.828 0.082 2.000 0.459 0.035 0.494 15.494 4.00 566a 1 Fe"/Fetot sample Mg/Fe" Si02 Al203 Ti02 Fe203 Fe0 Cr203 Mn0 Mg0 Ca0 Na20 K20 M1-M3 Ti Fe<sup>3+</sup> Mg Fe<sup>2+</sup> Mn Ng Pe2+ Pot Sum Si Ę Ca MA Na

		0	1
ABLE 5	-	Contin	ued

1.0				PLA	GIOCLASE	AMPHIBOLI	TES			
Sample	311C	311B	552	545	306	305	308	311A	546	1236
SiO2	43.47	44.17	42.32	46.70	41.54	42.52	45.83	40.63	45.25	43.45
A1203	14.56	13.71	14.29	9.42	12.97	13.68	10.83	14.06	10.94	11.91
TiO2	0.35	0.44	0.34	0.60	1.11	0.80	0.67	0.68	0.75	0.76
Fe203	2.35	3.09	3.40	2.47	3.03	3.65	2.91	5.70	2.93	5.15
FeO	11.10	11.86	13.07	10.83	15.45	13.99	11.17	16.25	12.03	13.20
Cr203	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.09	0.00
MnO	0.20	0.14	0.08	0.16	0.30	0.16	0.17	0.12	0.27	0.28
MgO	12.25	12.06	10.12	13.70	8.65	9.95	11.66	7.18	11.97	10.61
CaO	10.61	10.75	11.26	12.37	11.45	11.32	11.92	10.45	11.55	12.09
Na <sub>2</sub> O	1.71	1.55	1.60	1.30	1.67	1.35	1.23	1.58	1.30	1.60
K20	0.13	0.13	0.08	0.70	0.69	0.17	0.55	0.10	0.32	0.08
Tot	96.73	97.90	96.56	98.25	96.86	97.59	97.04	96.75	97.40	99.13
Fe"/Fetot	0.84	-	-	0.83	0.85	-	0.81	0.76	0.82	0.74
Si	6.382	6.437	6.322	6.786	6.308	6.320	6.741	6.200	6.658	6.384
Al	1.618	1.563	1.678	1.214	1.692	1.680	1.259	1.800	1.342	1.616
Al	0.901	0.792	0.837	0.399	0.628	0.716	0.618	0.728	0.554	0.446
Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.012	0.000	0.010	0.000
Ti	0.039	0.048	0.038	0.066	0.127	0.089	0.074	0.078	0.083	0.084
Fe <sup>3+</sup>	0.260	0.339	0.382	0.270	0.346	0.408	0.322	0.654	0.324	0.569
Mg	2.679	2.618	2.252	2.965	1.957	2.203	2.555	1.632	2.623	2.322
Fe <sup>2+</sup>	1.121	1.203	1.491	1.301	1.942	1.583	1.374	1.908	1.405	1.578
Mn	0.000	0.000	0.000	0.000	0.000	0.000	0.021	0.000	0.000	0.000
M1-M3	5.000	5.000	5.000	5.000	5.000	5.000	4.975	5.000	5.000	5.000
Mg	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe <sup>2+</sup>	0.241	0.242	0.141	0.015	0.019	0.156	0.000	0.165	0.075	0.043
Mn	0.025	0.017	0.010	0.020	0.039	0.020	0.000	0.016	0.034	0.035
Ca	1.668	1.678	1.801	1.925	1.862	1.802	1.878	1.708	1.820	1.903
Na	0.066	0.063	0.048	0.040	0.080	0.022	0.122	0.112	0.071	0.019
M <sub>4</sub>	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Na	0.421	0.375	0.416	0.326	0.411	0.367	0.228	0.355	0.299	0.436
к	0.024	0.024	0.015	0.130	0.134	0.032	0.103	0.019	0.060	0.015
A	0.445	0.399	0.431	0.455	0.545	0.399	0.331	0.375	0.359	0.451
Sum	15,445	15.399	15.431	15.455	15.545	15.399	15.306	15.375	15.359	15.451
Mg/Fe"	1.97	1.81	1.38	2.25	1.00	1.27	1.86	0.79	1.77	1.47

### Amphibole

Twenty-three analyses of amphiboles (22 calcic clinoamphiboles and one orthorhombic) are presented in table 5.

Some little compositional variations in the amphiboles belonging to the same thin section were detected during the microprobe analyses; however, because they did not appear related neither to zoning nor to optically-recognizable different amphiboles, they have been neglected in this paper and the compositions presented in table 5 are the average of 5-15 spot analyses.

A peculiar case is represented by sample no. 549, consisting of more than 98% amphibole and carrying few relics of Cpx and Grt; in this rock large compositional variations have been detected in amphibole crystals placed in different spatial position in respect to the relict phases. Analysis 549a is an average of 6 spotanalyses of the most abundant amphibole, whereas analyses nos. 549b and 549c represent compositions of crystals only slightly optically different from the main amphibole, but placed near Cpx and Grt, respectively.

The  $Fe^{2+}/Fe_{tot}$  ratio, chemically determined for 9 amphiboles, ranges from 0.74 to 0.85; the mean value of 0.81 has been assumed for all the other amphiboles. The cation proportions have been calculated on the anhydrous basis of 23 oxygens according to LEAKE (1977).



Fig. 5 - Classification of Ca-amphiboles according to LEAKE (1977).

5a: classification of amphiboles with:  $(Ca+Na)_{M4}>1.34;\ Na_{M4}<0.67;\ (Na+K)_A<0.50$  and Ti <0.50.

5b: classification of amphiboles with:  $(Ca+Na)_{M4}>1.34;~Na_{M4}<0.67;~(Na+K)_A>0.50;~Ti<0.50$  and  $Fe^{3+}<Al^{VI}.$ 

As can be seen from table 5, in all samples but two, the sum  $M_1$ - $M_3$  is 5; in some samples from ultramafic rocks, cation contents at the  $M_4$  site are slightly higher than 2 at.p.f.u.

According to LEAKE (1977) the majority of the amphiboles of the ultramafic rocks plot in the field of mg-hornblende (fig. 5a), whereas those of plagioclase amphibolites range in composition from mg-hornblende through ts-hornblende up to fe-tschermackite. Four amphiboles (3 from U.A. and 1 from P.A.), characterized by (Na+K) contents at the A-site higher than 0.50, plot in four different fields (fig. 5b): ed-hornblende, prg-hornblende, ferroanpargasite and ferroan-pargasitic-hornblende, respectively.

The Ti content of the calcic amphiboles is low and tends to be slightly higher in the plagioclase amphibolites. The K content



Fig. 6 - Al^IV versus  $\Sigma(Al^{VI}\text{-}Cr\text{-}Fe^3\text{-}2\text{Ti})(a)$  and Al^IV versus  $(Na+K)_A(b)$  plots for Hbl. (Same symbols as fig. 2).

is also generally very low. The Mg/Fe ratio in Ca-amphiboles gradually decreases from ultramafic to plagioclase amphibolites, in a similar way to the Mg/Fe ratio of the host rock. The Na content at the  $M_4$ -site is very low and generally lacking in the amphiboles of the ultramafic rocks.

The most relevant compositional differences between amphiboles from U.A. and P.A. refer to the Mg/Fe ratio (fig. 5) and to the heterovalent isomorphous substitution pattern.

In particular, as can be seen in fig. 6, the increase of  $AI^{IV}$  is mainly balanced by the increase of the A-site occupancy, in amphiboles of U.A., and by the increase of high-charge octahedral cations in amphiboles of P.A.

The orthorhombic amphibole (566b in table 5), characterized by low Al and Ca contents, and by a Mg/Mg+Fe ratio of 0.77, can be classified as anthophyllite (LEAKE, 1977).

## Spinel

Nine analyses of spinels of ultramafic rocks are presented in table 6.

The cationic proportions have been calculated on the basis of 8 oxygens, assuming a  $Fe^{3+}/Fe^{2+}$  ratio such as the sum of trivalent cations+Si is four.

 TABLE 6 - Microprobe analyses and structural formulae of spinels from ultramafic amphibolites.

Sample	556a	556b	555	551	572	310	553	548	550	549
SiO2	0.18	0.15	0.11	0.18	0.20	0.10	0.09	0.06	0.14	0.06
A1203	62.68	62.61	60.55	60.67	60.53	63.05	59.61	61.52	60.49	60.11
TiO2	0.00	0.02	0.02	0.03	0.00	0.00	0.00	0.01	0.01	0.00
Fe203	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FeO	23.82	23.74	26.41	27.69	25.65	23.60	27.28	27.69	27.04	31.26
Cr203	0.00	0.89	0.81	0.15	0.87	0.00	0.00	0.00	0.00	0.00
MnO	0.15	0.15	0.21	0.21	0.35	0.02	0.11	0.14	0.12	0.32
MgO	12.84	12.38	11.35	10.20	12.56	14.25	12.03	11.59	12.75	8.21
Tot	99.67	99.94	99.46	99.13	100.16	101.02	99.12	101.01	100.55	99.96
Formula	basis 8	oxygens								
Si	0.010	0.008	0.006	0.010	0.011	0.005	0.005	0.003	0.008	0.003
Al	3.911	3.890	3.833	3.881	3.784	3.862	3.790	3.845	3.777	3.879
Ti	0.000	0.001	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.000
Fe <sup>3+</sup>	0.079	0.092	0.160	0.108	0.205	0.133	0.205	0.152	0.215	0.118
Fe <sup>2+</sup>	0.976	0.956	1.026	1.149	0.932	0.892	1.023	1.076	0.983	1.313
Cr	0.000	0.037	0.035	0.006	0.037	0.000	0.000	0.000	0.000	0.000
Mn	0.007	0.007	0.010	0.010	0.016	0.001	0.005	0.006	0.005	0.015
Mg	1.013	0.974	0.909	0.825	0.992	1.104	0.966	0.915	1.006	0.670
Sum	5.996	5.974	5.980	5,990	5.977	5.997	5.994	5.997	5.994	5,998
Mg/Fe"	1.038	1.019	0.886	0.718	1.064	1.238	0.944	0.850	1.023	0.510

The sum of divalent cations (2.00-2.02 at.p.f.u.) is closed to the ideal value of 2. The spinels contain some  $SiO_2$  (0.06-0.18%) and very little  $TiO_2$ . Cr is present in appreciable amount only in two samples.

The trivalent cations consist mainly of Al (3.78-3.91 at.p.f.u.).

These minerals are members of the spinel s.s.-hercynite series with a hc content ranging from 66 to 45%.

### Chlorite

Six analyses of chlorites from ultramafic rocks are presented in table 7.

Sample	566	556	555	551	572	550
SiO2	29.21	28.72	28.75	28.85	30.15	26.63
A1203	20.71	21.75	21.58	19.68	19.74	20.88
TiO2	0.09	0.04	0.03	0.04	0.00	0.02
FeO	7.91	7.88	8.92	9.07	8.92	8.45
Cr203	0.00	0.00	0.00	0.00	0.00	0.00
MnO	0.00	0.00	0.00	0.00	0.00	0.00
MgO	27.83	28.16	28.85	27.75	27.71	31.96
CaO	0.00	0.00	0.00	0.00	0.00	0.00
Tot	85.75	86.55	88.13	85.39	86.52	87.94
Formula b	asis 28 oxy	gens				
Si	5.710	5.566	5.509	5.710	5.866	5.147
AlIV	2.290	2.434	2.491	2.290	2.134	2.853
AlVI	2.481	2.533	2.382	2.300	2.391	1.902
Ti	0.013	0.006	0.004	0.006	0.000	0.003
Fe	1.293	1.277	1.429	1.501	1.451	1.365
Cr	0.000	0.000	0.000	0.000	0.000	0.000
Mn	0.000	0.000	0.000	0.000	0.000	0.000
Mg	8.104	8.129	8.235	8.182	8.030	9.202
Sum	19.891	19.945	20.050	19.989	19.872	20.472
Mg/Fe"	6.269	6.367	5.763	5.451	5.535	6.739

 
 TABLE 7 - Microprobe analyses and structural formulae of chlorites from ultramafic amphibolites.

The cation contents, based on 28 oxygens (that is assuming eight  $H_20$  per formula unit) range from 19.27 to 20.47, in fairly good agreement with the ideal value of 20.

The Al<sup>IV</sup>/Al<sup>VI</sup>ratios are consistently close to unity. The Si ranges from 5.15 to 5.87 at.p.f.u. and the Mg/Fe ratios range from 0.84 to 0.87. These chlorites are all very similar and are intermediate between clinochlore and sheridanite (see fig. 7, after Hey, 1954).



Fig. 7 - Classification of chlorite according to Hey (1954).

#### Plagioclase

Eight analyses of plagioclases (6 from amphibolitic rocks and 2 from migmatites) are reported in table 8.

The total cation contents, based on 8 oxygens (4.96-5.01 at.p.f.u.), closely approach the ideal value of 5.

In spite of the good cation sums and the good closure of the analyses, we observe that (Si+Al) is generally higher than 4 (4.00-4.02 at.p.f.u.) and that (Na+Ca+K) tends to be lower than 1 (0.94-1.01 at.p.f.u.). This is probably due to slight alteration.

The composition of the amphibolitic plagioclase, expressed in terms of an-ab substitution, ranges from an<sub>89</sub>-ab<sub>11</sub> to an<sub>59</sub>-ab<sub>41</sub> (see fig. 8). The K content is very low.

The plagioclases of the migmatites have a slightly higher K content and their average composition is an<sub>22</sub>-ab<sub>76</sub>-or<sub>2</sub>.

### Biotite-Muscovite-K-feldspar-Kyanite

Analyses of two biotites, two muscovites, one K-feldspar and one kyanite from the migmatitic rocks are presented in table 9.

	P.A.								м.	
Sample	311B	545	306	305	308	311A	546	1236	568	543
SiO2	52.79	51.83	53.56	46.83	46.63	47.50	48.60	46.49	63.22	61.83
A1203	30.19	31.66	29.75	34.89	35.22	34.39	33.18	34,90	23.57	24.48
CaO	12.24	13.22	11.85	16.84	17.40	16.63	15.95	18.27	4.23	4.44
Na <sub>2</sub> O	4.56	3.69	4.56	1.64	1.47	2.14	2.22	1.31	8.35	8.80
к20	0.03	0.13	0.08	0.00	0.02	0.03	0.01	0.00	0.37	0.25
Tot	99.81	100.53	99.80	100.20	100.74	100.69	99.96	100.97	99.74	99.80
Formula	basis 8	oxygens								
Si	2.393	2.337	2.423	2:141	2.125	2.163	2.221	2,119	2,795	2.742
Al	1.613	1.682	1.586	1.880	1.891	1.845	1.786	1.875	1.228	1,279
Ca	0.594	0.638	0.574	0.825	0.849	0.811	0.781	0.892	0.200	0.211
Na	0.401	0.322	0.400	0.145	0.130	0.189	0.197	0.116	0.715	0.756
K	0.002	0.007	0.005	0.000	0.001	0.002	0.001	0.000	0.021	0.014
Sum	5.002	4.987	4.987	4.991	4.995	5.010	4.985	5.001	4.959	5.003
Ca Ca+Na+K	0.596	0.659	0.587	0.850	0.866	0.810	0.798	0.885	0.214	0.215

 
 TABLE 8 - Microprobe analyses and structural formulae of plagioclases from plagioclase amphibolites and migmatites.

The two biotites have very similar compositions. The structural formulae, calculated on the basis of 22 oxygens, are characterized by relatively low sum of octahedral cations (5.61-5.66 at.p.f.u.), slight deficiency of interlayer cations (both 1.82 at.p.f.u.) and Mg/Fe ratios typical of Fe-biotites.



Fig. 8 - Na-K-Ca plot for feldspars (filled circles = plagioclase amphibolites; filled squares = migmatites).

	в	io	м	u		Kfs	Ку
Sample	568	543	568	543	. F	543	568
Si02	35.64	34.45	46.39	45.06	SiO <sub>2</sub>	63.22	37.06
A1203	20.73	20.81	36.03	34.47	A1203	20.51	64.07
TiO2	2.52	2.43	0.86	0.65	FeO	0.00	0.21
FeO	18.79	20.01	1.11	1.32	MgO	0.00	0.00
MnO	0.26	0.25	0.00	0.00	CaO	0.05	0.00
MgO	8.55	7.69	0.77	0.92	Na <sub>2</sub> O	1.14	0.00
CaO	0.07	0.08	0.01	0.07	K20	14,19	0.00
Na <sub>2</sub> O	0.13	0.12	0.47	0.45	STO	0,08	0.00
K20	9.27	9.08	10.29	10.12	BaO	0.43	0.00
Tot	95.96	94.92	95.93	93.06	Tot	99.62	101.34
Formula	basis 22	oxygens			8 oxygens		5 oxygens
Si	5.353	5.273	6.116	6.140	Si	2.922	0.988
Al	2.647	2.727	1.884	1.860	Al	1.117	2.013
AL	1.021	1.027	3.714	3.674	Fe	0.000	0.005
Ti	0.284	0.280	0.085	0.067	Ca	0.002	0.000
Fe	2.359	2.561	0.122	0.150	Na	0.102	0.000
Mn	0.033	0.032	0.000	0.000	Cr.	0.030	0.000
Mg	1.913	1.753	0.151	0.187	Ba	0.002	0.000
Ca	0.011	0.013	0.001	0.010	ba	0.000	0.000
Na	0.038	0.036	0.120	0.119			
K	1.775	1.772	1.730	1.758			
Sum	15.435	15.474	13.925	13.965	Sum	4.989	3.006
Mg/Fe"	0.811	0.685	1.236	1.242	K K+Na+Ca	0.888	·

TABLE 9 - Microprobe analyses and structural formulae of biotites, muscovites,K-feldspar and kyanite from migmatites.

The two muscovites too are very similar in composition. Based on structural formulae calculated assuming 22 oxygens, the Si contents range between 6.12-6.14 at.p.f.u. and the sum of octahedral cations is, in both cases, 4.07 at.p.f.u. and is given predominantly by Al (92%).

The interlayer cations are slightly deficient (1.85-1.89 at.p.f.u.) and consist essentially of K; Na is relatively low (0.12 in both cases) and Ca is negligible.

The K-feldspar of rock 543, in spite of the good closure of the chemical analysis and of the sum of the cations (4.99 at.p.f.u., on the basis of 8 oxygens), exibits a high value of Al (1.12 at.p.f.u.) and a relatively low sum of ten-fold coordinated cations (0.95 at.p.f.u.). This, similarly to the plagioclases of migmatites, may be due to the incipient kaolinization of the mineral. The structural state is that of orthoclase.

This orthoclase contains very low quantities of Ca and Sr; the Na content is also low (0.10 at.p.f.u.; see fig. 8) and BaO is present in appreciable amount (0.43%).

The only kyanite analysis is close to stoichiometric composition  $Al_2SiO_5$ ; the sum of cations, based on five oxygens, is 3.00.

#### ELEMENT PARTITIONING

After the pioneering works of RAMBERG and DE VORE (1951), the study of the disproportion of elements between coexisting phases received increasing interest, so that, in the following years, the model of solid solution, especially for cristallochemically simple minerals, became gradually more elaborated and detailed (for a general survey, see SAXENA, 1973).

More recently, due in part to X-ray diffractometry, the studies of the intracrystalline elemental partition have opened new fields of investigation, which are of common interest of both petrologist and crystallochemist.

Unfortunately, complex solid solutions, such as those of the minerals of the present study, have remained more difficult to treate quantitatively, and non-ideal solid-solution models are not available for most of the minerals.

However, for the purpose of this paper, it will suffice to assume an ion-for-ion type of ideal fractionation, bearing in mind that the solution behaviours markedly deviate from such a distribution model.

The partitioning of Mg and  $Fe^{2+}$  between pairs of minerals are illustrated in figs. 9, 10a and 10b.

Fig. 9 shows the  $Mg/Fe^{2+}$  distribution among Grt, Ol, Opx and Cpx of the ultramafic amphibolites, whereas fig. 10a shows the  $Mg/Fe^{2+}$  distribution for all the phases (both in ultramafic and plagioclase amphibolites) in respect to Hbl (which is a common phase in all the rocks).

Fig. 10b compares Hbl and amphibolite-facies phases. KD have been calculated as an average value as follows:  $KD_{Mg-Fe} = (Mg/Fe)_{n/2}/(Mg/Fe)_{B}$ .

The main results of this study are:

a) In the ultramafic amphibolites the limited number of coexisting pairs does not allow a direct estimation of KD among all the phases of the primary granulite-facies paragenesis. However the order of Mg/Fe enrichment appears as follows: (Mg/Fe) Cpx  $^{2.39}$ 



Fig. 9 - Magnesium-ferrous iron partitioning between coexisting pairs of granulitefacies mafic silicates from ultramafic amphibolites. Values of KD is also shown.

 $Opx \stackrel{1.33}{>} Ol \stackrel{2.7}{>} Grt$ . And thus a  $KD^{Cpx-Grt}$  of 8.6 can be calculated, which is similar to that measured on the Cpx-Grt pair of sample 549 ( $KD^{Cpx-Grt} = 9.1$ ). Evidently the eight-fold coordinated site of Grt strongly concentrates  $Fe^{2+}$  in respect to the smaller six-fold coordinated site of Cpx.

b) Hbl concentrates iron relative to Cpx (KD = 1.53) and Mg relative to Opx, Ol, Grt (see fig. 10a).

 $KD^{Grt-Hbl}$  is higher (0.27) in plagioclase amphibolites than in the ultramafic ones (0.20), whereas the opposite is apparent for  $KD^{cpx-Hbl}$  (see fig. 10a).

c) Among the ferromagnesian phases formed during the amphibolite-facies metamorphism (fig. 10b), ferrous iron is concentrated in Spl relative to Hbl ( $KD^{Spl\cdotHbl} = 0.22$ ), Ath and Chl. The partition of Mg, Fe and Al between Hbl, Spl and Chl is shown in fig. 11.





Fig. 10 - Magnesium-ferrous iron partitioning between granulites-facies minerals and Hbl (10a) and between coexisting pairs of amphibolite-facies minerals (10b) (same symbols as fig. 2).

d) The Mg/Fe partition between Hbl and Grt or Cpx, which are phases in evident textural disequilibrium, is relatively systematic both for ultramafic and plagioclase amphibolites and appears to be more regular than that between phases formed during the same amphibolitic event and showing textural equilibrium (Hbl-Chl; Hbl-Spl) (compare figs. 10a and 10b).

e) Fig. 3 shows the relations of Hbl, the main mineral product of the amphibolite-facies metamorphism, with the reactant phases, in terms of Ca-Mg-Fe and Al-Mg-Fe.

Ca is fairly constant for all the amphiboles, even if, on average, a lower content can be observed in Hbl of ultramafic amphi-



Fig. 11 - Al-Mg-Fet partitioning between amphibolite-facies minerals of ultramafic amphibolites. Tie-lines join coexisting phases (after GHEZZO et al., 1980).

bolites, reflecting the relatively high Fe occupancy of  $M_4$  site, possibly because, among the relics, Ca-poor phases like Ol and Opx, generally persist.

The variation of total Al content is notably more marked and, in particular, one can note that, when Grt persists among the relict phases, Hbl has higher Al content (and in general higher Fe/Mg ratio), whereas the lower Al content in Hbl is achieved when Cpx is still present in the assemblage.

The field outlined for Hbl in fig. 3b should be seen as the limit of miscibility, essentially in terms of Al over- and undersaturation, of calcic amphiboles at these P-T conditions.

The broad compositional range shown by the rock 549 (549b and 549c in fig. 3b) can be clearly related to the contact with relict Cpx and Grt respectively; the compositional variations occurring in this sample will be discussed in a specific paper, with the aid of single-crystal X-ray diffractometry (manuscript in preparation).

f) The Na content of Hbl in plagioclase-bearing rocks should reflect equilibrium between the two minerals (SPEAR, 1980, 1981). As can be seen in table 5 the amount of Na in  $M_4$  site is negligible, whereas the Na occupancy of the A-site is variable in different samples (0.23-0.44).

The variation of Na occupancy of the A-site  $(X_{Na, A})$  in relation to  $X_{ab, Pl}$  is shown in fig. 12, which, according to SPEAR (1981), should illustrate, in Qtz-bearing samples, the equilibrium tr + ab = ed + 4qtz, at different temperatures.



Fig. 12 - Plot of  $X_{ab}$  in plagioclase versus  $X_{Na, A}$  in amphibole (filled circles) and  $X_{(Na, A+Na, M_d)}$  (crosses) for plagioclase amphibolites. After SPEAR (1981).

In this diagram, the distribution of samples is not highly regular, as several of them plot in the field of plagioclase miscibility gap, possibly because not all the rocks contain Qtz. A better distribution, (crosses in fig. 12), suggesting equilibrium temperature between 600 and 725°C, can be obtained if we attribute to the Asite all the sodium present in the amphibole analysis as indicated by X-ray refinement data (manuscript in preparation).

g) Regarding the element partitioning between coexisting phases of migmatites, Grt concentrates Mn and Fe relative to Bio and Ms ( $KD^{Grt\cdot Bio} = 0.21$ ;  $KD^{Grt\cdot Ms} = 0.13$ ) and Bio concentrates iron relative to Ms ( $KD^{Ms\cdot Bio} = 1.66$ ).

The Na/K partition appears as follows: Kfs > Ms > Bio; whereas KD<sup>pl-Kfs</sup> has a value of 27.7. The partition coefficient of Ca between Grt and Pl, expressed as  $K_{Ca}^{Grt-Pl} = (Ca/Ca + Mg + Fe + Mn)_{Grl}/(Ca/Ca + Na + K)_{pl}$ , ranges from 0.16 to 0.19.

Most of the equilibria discussed in this section are normally used for geothermometry and/or geobarometry (Cheney and Guidotti, 1979; Dahl, 1980; Danckwerth and Newton, 1978; Evans and Frost, 1975; Ferry and Spear, 1978; Ghent, 1976; Ghent and Stout, 1981; Hodges and Spear, 1982; Raheim and Green, 1974; Saxena, 1979; Spear, 1980, 1981; Stormer and Whitney, 1978; Thompson, 1976).

However, because of the non-ideal solution behaviour of most minerals and of the uncertainties regarding the role of diffusional processes in mineral phases during the uplift and cooling of the basement, we consider, at present, of scarce significance the estimate derived from exchange geothermometers and geobarometers applied to such a limited number of rocks, which show evidence that the mineral systems were not istantaneously quenched.

#### DISCUSSION

Some considerations regarding the various minerals and the problems still remained unsolved will be discussed below.

# Granulite-facies minerals

1) Cpx and Opx have textural appearance of relict phases, but their compositional features (in particular their low Al content, and the low Na content of Cpx) are not typical of granulite-facies pyroxenes; they were probably re-equilibrated during the amphibolite-facies metamorphism.

2) Possibly, a similar re-equilibration occurred also for olivine and plagioclase.

Grt (especially in ultramafic amphibolites), should be the only granulite-facies phase which has maintained some primary compositional characters, taking into account the high Ca content of some samples.

4) Hbl, in ultramafic amphibolites, contains up to 2% Na<sub>2</sub>O, and none of the relict phases contains significant amount of Na<sub>2</sub>O. Was Na present in the granulitic clinopyroxene or in a primary Na-rich amphibole?

## Amphibolite-facies minerals

5) Hbl, the main product mineral, shows large compositional variations in different samples and, sometimes, within the same sample. Because geologic and petrologic evidence suggest that Hbl formed, in the different assemblages, during a single metamorphic event, the observed compositional variations cannot be explained in terms of P, T changes.

Indeed, these compositional variations appear strictly dependent upon both those of the reactant system (nature and proportion of the phases) and the equilibria among the new phases (manuscript, in preparation).

6) In ultramafic amphibolites the influence of Spl and Chl on Hbl is negligible and tends to slightly modifie the partition of Mg and Fe; the chemical composition of Hbl appears to be controlled by the Grt-Cpx proportion in the reactant system. Another important influence is probably of crystallochemical nature, taking into account that Hbl incorporates at the A-site all the sodium of the rock and thus determining the amount of the Al<sup>IV</sup>-Si substitution (see fig. 6).

7) In plagioclase amphibolites too, the chemical composition of Hbl is influenced, not only by the nature and proportion of reactant phases (mainly Grt and Cpx), but also by the equilibria operating on Hbl-Pl pair (see for instance SPEAR, 1980; 1981).

8) A worth noting feature is the good Mg/Fe partition between Hbl and phases showing apparent textural disequilibrium (Grt and Cpx). This may simply reflect the fact that Hbl, being the main product phase, tends to assume the Mg/Fe ratios of the host rocks; however it cannot be excluded that, during the amphibolite-facies metamorphism, Mg/Fe cation exchange reactions operated on both old and new phases, determining a new Mg/Fe equilibrium.

9) It emerges from above that, during the amphibolite-facies metamorphism, different retrogressive reactions operated in different rock systems according to the following scheme:

 $Cpx+Grt+Opx+Ol_1+Na-Ti rich Amph(?)+H_2O =$ 

 $= Hbl+Chl+Spl+Ol_{2} \quad (U.A.)$ Cpx+Grt<sub>1</sub>+Pl<sub>1</sub>+H<sub>2</sub>O=Hbl+Pl<sub>2</sub>+Cpx+Grt<sub>2</sub> (P.A.) The possibility of re-equilibrium and the consequent uncertainties regarding the nature and the composition of the reactant phases (see points 1-4) hamper a more precise definition of the amphibolite-facies reactions.

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