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## **Amphiboles' Chemistry as Pressure and Temperature Indicator in Amphibolites from the Serbo-Macedonian Massif (Greece)**

by *A. Kassoli-Fournaraki, G. Eleftheriadis and K. Michailidis\**

### **Abstract**

The amphiboles' chemistry from amphibolites of the Serbo-Macedonian massif is examined in relation to P, T conditions of metamorphism. The studied rock samples display the "common" assemblage amphibole + plagioclase + quartz + epidote + sphene + apatite + chlorite  $\pm$  garnet  $\pm$  Fe<sup>3+</sup>-oxide  $\pm$  pyroxene. Plotting of amphibole formula proportions in a number of discriminant diagrams reveals low-P conditions for the rocks in study and a mostly coincidence with Abukuma high-temperature, low-pressure metamorphic facies series type.

**Keywords:** amphibole, igneous origin, mafic schist, mineral assemblage, low-pressure conditions.

### **INTRODUCTION**

Up to now mafic rocks can not be used with success in defining physical conditions of metamorphism as pelitic rocks can do. Since the mineralogy of pelitic rocks changes even with small increments of pressure and temperature the metamorphic grade can relatively easily be defined by means of resulting key minerals. Yet, this is not easy to happen with mafic schists where a much more detailed mineral and chemical composition has to be determined.

In this paper the definition of a possible metamorphic grade and relative P, T conditions is attempted for the amphibolitic rocks of Serbo-Macedonian massif on the basis mainly of their amphiboles' chemistry.

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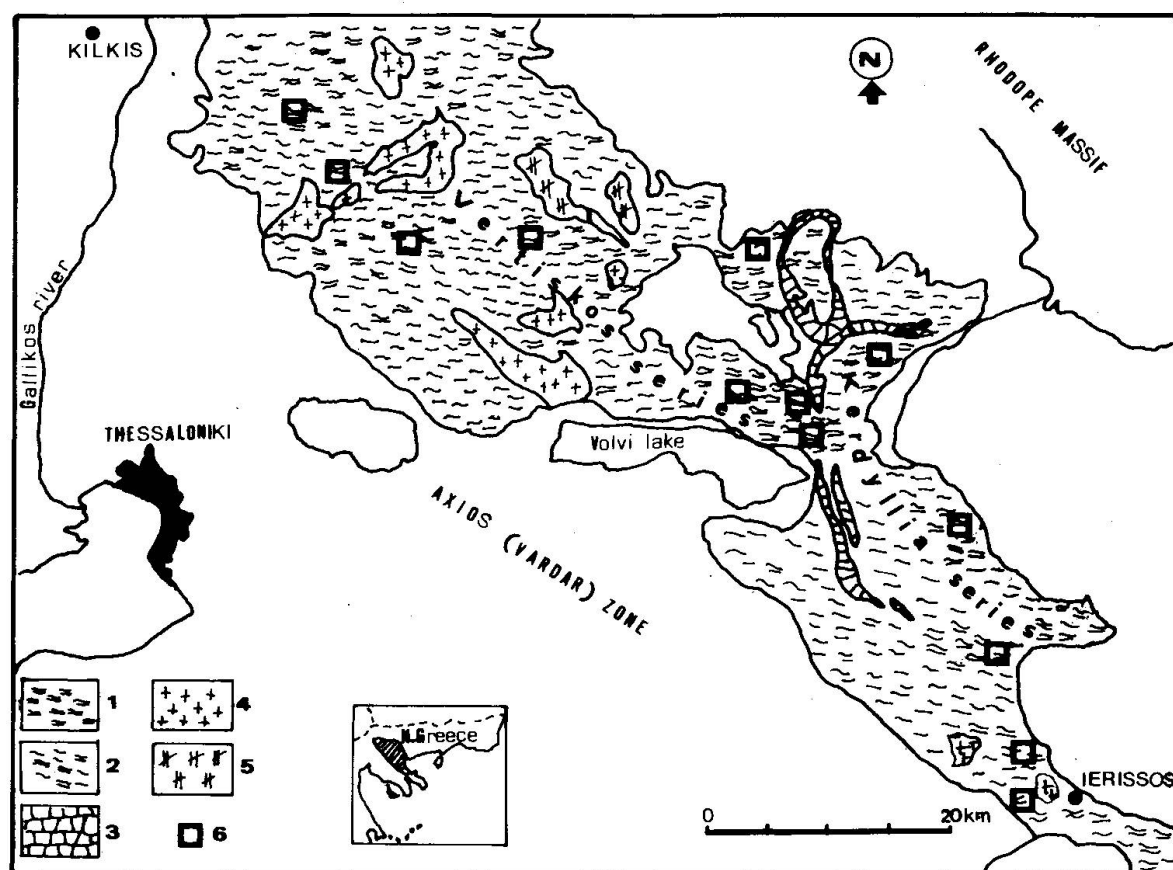


Fig. 1 Location sketch map of the amphibolitic samples in Serbo-Macedonian massif. 1 = Amphibolites. 2 = Alternation of gneisses and amphibolites. 3 = Marbles. 4 = Granites. 5 = Quartz diorites. 6 = Sample locations.

The Serbo-Macedonian massif has been recently the subject of research for many investigators because of the interest which it displays. It shows a quite complicated lithology and evolution.

The Greek part of the Serbo-Macedonian massif has been divided by KOCKEL et al. (1971, 1977) into two series (Fig. 1); a) the upper Vertiskos series to the west consisting of a complicated lithology, mainly gneisses, mica schists and amphibolites interrupted by meta-ophiolites and ultra-basic rocks, and b) the lower Kerdyllia series composed largely of migmatic gneisses and amphibolites intercalated with marble units. Figure 1 presents the location map of the studied amphibolitic samples in the present paper.

The genesis, geological setting, petrography, magma type, and tectonic setting of these amphibolitic rocks have been studied in KASSOLI-FOURNARAKI (1981) and SAPOUNTZIS et al. (in press). The data indicated that the amphibolites under consideration displayed an igneous origin and were derived from a magma of tholeiitic to olivine-tholeiitic composition with chemical affinities to ocean-floor basalts. They possibly consist a part of an ophiolite sequence and their last metamorphism took place in Lower to Middle Cretaceous.

## MINERAL ASSEMBLAGES

The mineral constituents of the rocks in study are primarily amphibole, plagioclase (calcic oligoclase to andesine) and quartz followed usually by small amounts of epidote, zoisite, sphene, apatite, secondary chlorite and in some cases by garnet, pyroxene (diopside), biotite or other accessories. The amphiboles, according to LEAKE'S (1978) nomenclature, were mainly characterized as magnesio-hornblendes. Smaller numbers fall in the areas of tschermakitic-edenitic-, ferroan pargasitic- and magnesian hastingsitic hornblendes (KASSOLI-FOURNARAKI et al. (in press).

It is known that mafic schists contain albite, chlorite, clinozoisite or epidote and actinolite in the greenschist facies, changing to plagioclase ( $An > 20\%$ ) and aluminous hornblende in the amphibolite facies with some epidote in certain cases. They also contain sphene (or another Ti-bearing phase) + quartz  $\pm$  iron oxide  $\pm$  K-mica. It has been proved (MOODY, 1979) that in both the oceanic and continental environments, metamorphic assemblages from rocks of mafic compositions have the same mineralogy: amphibole + chlorite + epidote + plagioclase + quartz + Ti-phase  $\pm$  carbonate  $\pm$  K-mica  $\pm$  Fe<sup>3+</sup>-oxide. This made LAIRD (1980) and LAIRD and ALBEE (1981) to propose the "Common" assemblage for mafic schists.

The amphibolitic rocks of the present study are typical products of regional metamorphism. Mineral parageneses as well as plagioclase composition determine an amphibolite facies for the rocks in study. Within the limits of the amphibolite facies a slight increase of the P.T. conditions is deduced for the southeast areas of the zone.

## AMPHIBOLES' CHEMISTRY IN AMPHIBOLITES AS A FUNCTION OF P AND T

Studies of naturally occurring amphibolites have led to the conclusion that hornblende is sensitive in composition changes with increasing metamorphic grade (ENGEL and ENGEL, 1962b; BINNS, 1965a, b; LEAKE, 1965; COOPER and LOVERING, 1970; ERNST, 1972; GRAHAM, 1974; RAASE, 1974; GRAPES, et al., 1977; LAIRD and ALBEE, 1981; and others). This appears more obvious when the examined common hornblendes derive from rocks of highly diverse composition, recrystallized over a wide range of P and T. Amphiboles from the greenschist facies have always actinolitic composition, while Al- and Na-rich pargasites dominate in the amphibolite and granulite facies. Yet, things, are not always so clear since many times the bulk rock chemistry effects up to a point the amphibole composition. A contrasting exception to the above mentioned relation of amphiboles' chemistry to metamorphic conditions, has been referred by ENGEL



and ENGEL (1962) who describe hornblendes from Emeryville-Colton amphibolites not responsive to the recorded regional gradients in P, T and X.

Generally, the variation in composition of metamorphic amphiboles that has been mostly examined concerns the  $Al^{IV}/Al^{VI}$  partitioning and the Na<sup>A</sup>, Si and Ti contents in relation to the metamorphic grade. Much attention has been also paid to the Al/Si ratio. Usually, Al replaces larger amounts of Si, a little by little in the tetrahedral sites as temperature of metamorphism increases. Yet, the above consideration has not proved so with the Adirondack and Black Hills amphibolitic rocks. Possibly the variation in Al of metamorphic amphiboles is related to variations in Al of the host rock.

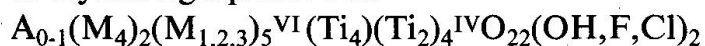
Using LAIRD'S and ALBEE'S (1981) diagrams and on the basis of the amphiboles' chemistry derived from rocks of the Serbo-Macedonian massif having the "Common" assemblage we tried to confirm the metamorphic grade. LAIRD'S and ALBEE'S data are quite reliable since pelitic assemblages interlayered with mafic schists were used to control the metamorphic grade.

#### ANALYTICAL PROCEDURE

Twenty eight chemical analyses of amphiboles derived from corresponding representative rock samples have been performed both by means of microprobe and wet chemical analysis (Table 1). The microanalyzer used was a Hitachi-Perkin Elmer XMA-5B type operated at 15 kV accelerating voltage, and with 20 nA specimen current. For standard referent materials pure metals as well as natural minerals were used. The correction program filed in a Univac 1100 System was made for the conditions of the specific instrument.

Wet chemical analyses were performed on a concentrate of pure and clear amphibole crystals.

The cation calculation and site assignment was made according to the method which gives total cations, except (Na + K + Ca) normalized to 13 (Table 1). The  $M_4$  site remains free of  $Fe^{2+}$ , Mg and Mn. This normalization was chosen because in no case  $Ca + Na_{M_4}$  was less or equal to 2. Besides, this method gives the maximum possible  $Fe^{3+}$  stoichiometrically and very reliable values for the rest cations. The method used for the site assignment was that of ROBINSON (1982) and the general formula used, translated into site terminology of crystallographers was:



The values derived from the above calculations were used in a number of the discrimination diagrams which follow. In the rest of the diagrams total cations were normalized to 16 with total iron as  $Fe^{2+}$ .

Tab. 1 Chemical analyses of the Serbo-Macedonian amphiboles.

	1	2	3	4	5	6	7	8	9	10
SiO <sub>2</sub>	41.80	45.12	49.30	44.81	44.30	42.86	42.20	43.75	45.84	43.84
TiO <sub>2</sub>	2.92	1.49	1.06	1.58	0.75	0.91	1.13	0.63	0.86	0.90
Al <sub>2</sub> O <sub>3</sub>	11.60	12.16	6.27	11.47	10.20	11.32	10.80	11.80	10.91	13.73
FeO <sub>tot</sub>	18.26	15.13	12.93	12.17	14.75	20.00	19.80	17.26	11.29	12.45
MnO	0.37	0.44	0.57	0.46	0.25	0.57	0.32	0.35	0.48	0.35
MgO	8.40	10.68	13.43	12.49	11.20	8.13	7.80	10.08	13.36	11.57
CaO	11.20	11.34	12.07	11.36	12.60	11.15	12.20	11.66	11.97	11.86
Na <sub>2</sub> O	1.90	1.52	0.69	2.06	1.50	1.55	2.00	2.40	1.48	1.44
K <sub>2</sub> O	0.50	0.61	0.41	0.50	0.20	0.63	0.50	0.67	0.58	0.66
Total	96.95	98.49	96.73	96.90	95.75	97.12	96.75	98.60	96.77	96.80
Si	6.335	6.552	7.217	6.567	6.687	6.463	6.513	6.471	6.688	6.428
Al <sup>IV</sup>	1.665	1.448	0.783	1.433	1.313	1.537	1.487	1.529	1.312	1.572
T	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
Al <sup>VI</sup>	0.408	0.634	0.299	0.549	0.502	0.475	0.478	0.529	0.564	0.802
Ti	0.333	0.163	0.117	0.174	0.085	0.103	0.131	0.070	0.094	0.099
Fe <sup>3+</sup>	0.299	0.418	0.191	0.289	0.089	0.679	0.016	0.349	0.291	0.311
Mg	1.897	2.311	2.930	2.728	2.519	1.827	1.794	2.222	2.905	2.528
Fe <sup>2+</sup>	2.016	1.420	1.392	1.203	1.773	1.843	2.539	1.786	1.087	1.216
Mn	0.047	0.054	0.071	0.057	0.032	0.073	0.042	0.044	0.059	0.044
M <sub>1</sub> -M <sub>3</sub>	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000
Ca	1.819	1.765	1.893	1.784	2.000	1.801	2.000	1.849	1.871	1.863
Na	0.181	0.235	0.107	0.216	-	0.199	-	0.152	0.129	0.137
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	0.377	0.193	0.089	0.369	0.439	0.254	0.598	0.536	0.290	0.272
K	0.097	0.113	0.077	0.093	0.039	0.121	0.098	0.126	0.108	0.123
Ca	-	-	-	-	0.038	-	0.017	-	-	-
A	0.474	0.306	0.166	0.462	0.516	0.375	0.713	0.662	0.398	0.395

Tab. 1 (Continued).

	11	12	13	14	15	16	17	18	19
SiO <sub>2</sub>	44.50	42.20	44.50	43.69	44.40	41.60	41.68	45.05	41.50
TiO <sub>2</sub>	0.55	0.58	0.67	1.17	0.75	0.75	1.77	0.54	1.05
Al <sub>2</sub> O <sub>3</sub>	10.40	13.60	9.20	11.15	10.20	10.80	12.19	12.81	10.80
FeO <sub>tot</sub>	15.32	14.04	15.93	16.57	11.97	18.00	18.70	9.56	18.09
MnO	0.17	0.19	0.37	0.65	0.33	0.34	0.58	0.27	0.43
MgO	11.50	10.80	11.20	10.54	13.60	9.70	8.80	14.72	9.20
CaO	12.20	12.20	12.20	11.30	12.60	12.40	11.62	12.83	12.60
Na <sub>2</sub> O	2.00	1.90	1.80	1.53	2.40	1.90	1.43	1.38	1.40
K <sub>2</sub> O	0.80	0.70	1.00	1.03	0.40	0.70	1.67	0.92	0.43
Total	97.44	96.21	96.87	97.63	96.65	96.19	98.44	98.08	95.50
Si	6.629	6.330	6.713	6.467	6.593	6.385	6.255	6.456	6.405
Al <sup>IV</sup>	1.371	1.670	1.287	1.533	1.407	1.615	1.745	1.544	1.595
T	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
Al <sup>VI</sup>	0.455	0.735	0.349	0.417	0.379	0.340	0.412	0.620	0.371
Ti	0.062	0.066	0.076	0.133	0.084	0.087	0.200	0.058	0.122
Fe <sup>3+</sup>	0.168	0.196	0.123	0.646	0.085	0.321	0.461	0.317	0.309
Mg	2.553	2.414	2.518	2.328	3.010	2.219	1.968	3.144	2.116
Fe <sup>2+</sup>	1.740	1.565	1.887	1.410	1.402	1.990	1.886	0.829	2.026
Mn	0.022	0.024	0.047	0.083	0.040	0.043	0.073	0.032	0.056
M <sub>1</sub> -M <sub>3</sub>	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000
Ca	1.947	1.961	1.972	1.792	2.000	2.000	1.868	1.970	2.000
Na	0.053	0.039	0.008	0.208	-	-	0.132	0.030	-
M <sub>4</sub>	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Na	0.525	0.514	0.519	0.231	0.691	0.565	0.284	0.353	0.419
K	0.152	0.134	0.192	0.194	0.076	0.137	0.320	0.168	0.085
Ca	-	-	-	-	0.005	0.039	-	-	0.084
A	0.677	0.648	0.711	0.425	0.772	0.741	0.604	0.521	0.588

Tab. 1 (Continued).

	20	21	22	23	24	25	26	27	28
SiO <sub>2</sub>	48.98	42.33	43.20	43.20	45.39	45.56	45.05	44.60	45.10
TiO <sub>2</sub>	0.74	1.46	0.75	1.26	0.99	1.08	0.94	0.43	0.63
Al <sub>2</sub> O <sub>3</sub>	8.40	11.85	10.80	12.02	10.49	9.99	8.94	9.00	9.50
FeO <sub>tot</sub>	10.68	17.36	16.83	14.93	14.08	16.00	16.67	13.40	13.95
MnO	0.37	0.53	0.36	0.74	0.54	0.47	0.47	0.30	0.26
MgO	14.81	9.88	10.00	11.45	12.46	11.68	11.26	13.70	12.30
CaO	12.67	12.07	12.60	11.78	13.66	12.27	11.83	13.00	12.40
Na <sub>2</sub> O	1.14	1.57	1.80	1.34	1.27	0.97	1.13	1.40	1.70
K <sub>2</sub> O	0.29	0.87	0.70	0.81	0.38	0.35	0.36	0.10	0.40
Total	98.08	97.92	97.04	97.53	99.26	98.37	96.65	95.93	96.24
Si	7.016	6.319	6.547	6.346	6.607	6.630	6.699	6.633	6.740
Al <sup>IV</sup>	0.984	1.681	1.453	1.654	1.393	1.370	1.301	1.367	1.260
T	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
Al <sup>VI</sup>	0.435	0.404	0.477	0.428	0.407	0.344	0.266	0.211	0.413
Ti	0.080	0.164	0.085	0.139	0.108	0.118	0.105	0.048	0.071
Fe <sup>3+</sup>	0.131	0.468	0.049	0.706	0.078	0.625	0.659	0.494	0.165
Mg	3.162	2.198	2.259	2.507	2.703	2.533	2.496	3.037	2.739
Fe <sup>2+</sup>	1.148	1.699	2.084	1.128	1.636	1.322	1.414	1.173	1.578
Mn	0.044	0.067	0.046	0.092	0.068	0.058	0.059	0.037	0.033
M <sub>1</sub> -M <sub>3</sub>	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000
Ca	1.945	1.931	2.000	1.854	2.000	1.913	1.884	2.000	1.985
Na	0.055	0.069	-	0.146	-	0.087	0.116	-	0.015
M <sub>4</sub>	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Na	0.262	0.385	0.529	0.236	0.358	0.187	0.210	0.404	0.478
K	0.053	0.166	0.135	0.152	0.071	0.065	0.068	0.019	0.076
Ca	-	-	0.046	-	0.131	-	-	0.072	-
A	0.315	0.551	0.710	0.388	0.560	0.252	0.278	0.495	0.554

# RELATION OF THE AMPHIBOLE'S CHEMISTRY IN STUDY TO METAMORPHIC FACIES

In Figure 2 A, C and D our amphiboles plot mainly in or near the region characterized by LAIRD and ALBEE as garnet zone. Only the ratios plotted in dia-

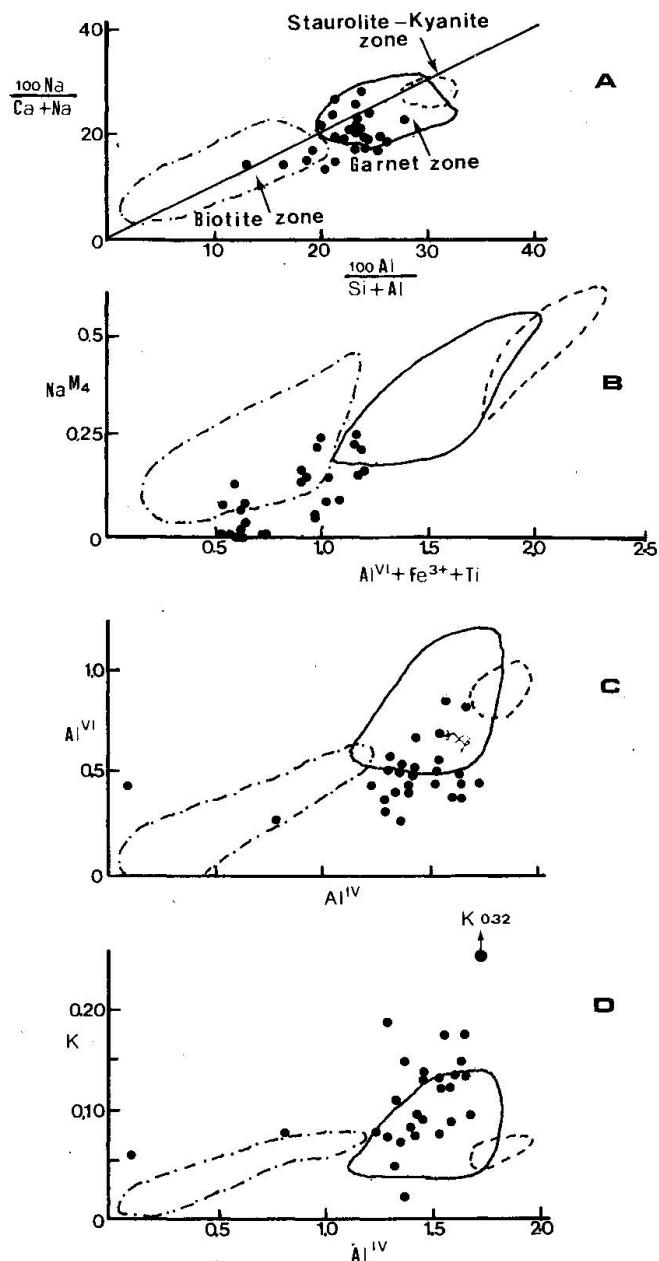


Fig. 2 Amphiboles formula proportion variation diagrams of Serbo-Macedonian massif amphibolitic rocks in relation to LAIRD's and ALBEE's (1981) defined zones. A: plot of total Na / (Ca + Na) vs total Al / (Si + Al). B: plot of  $\text{Na}^{\text{M4}}$  vs  $\text{Al}^{\text{VI}} + \text{Fe}^{3+} + \text{Ti}$ . C:  $\text{Al}^{\text{VI}}$  vs  $\text{Al}^{\text{IV}}$  and D: K vs  $\text{Al}^{\text{IV}}$ .

- - - - - Biotite zone  
 ————— Garnet zone  
 . . . . . Stauroilite-Kyanite zone

after LAIRD and ALBEE (1981)

gram A (total Na/(Ca + Na) vs total Al/(Si + Al) are independent of the stoichiometry. Diagram B does not give good results since the sum  $\text{Al}^{\text{VI}} + \text{Fe}^{3+} + \text{Ti}$  remains in lower values (0.5–1.2) than those referred by the above authors ( $\approx 1.2$ –2) and Na in  $\text{M}_4$  site is many times zero because of the high Ca values (sometimes  $> 2.00$ ).

SPEAR (1981) in his experiment study of hornblende stability and compositional variability in amphibolite (of olivine tholeiite composition) noticed that the cations in amphibole which display the largest temperature dependence are Al, Na, K and Ti. These at constant  $P_f$  and on a given oxygen fugacity buffer increase while Si decreases with increasing temperature. The same trend occurs at constant T and  $P_f$  with decreasing  $f_{\text{O}_2}$ .

LAIRD et al. (1984) separated the calcic amphibole analyses into groups based on facies series indicated by intercalated pelitic schist and amphibole composition in combination with plagioclase chemical changes. Plotting of our data in their suggested corresponding diagram (Fig. 3,  $\text{Al}^{\text{VI}} + \text{Fe}^{3+} + 2\text{Ti} + \text{Cr}$  vs  $\text{Na}_{\text{M}_4}$ ) shows them all in the area of Low P.

Figure 4 A, B, C and D present our amphibole analyses compared to the data for amphiboles from many different world-wide occurrences of mafic schist with the "Common" assemblage. These diagrams are used by LAIRD and ALBEE (1981) and the normalizations used are equal so that the data can be comparable. As it is obvious our amphiboles fall in the low pressure facies series represented by the Abukuma Plateau terrane in Japan (SHIDO, 1958; SHIDO and

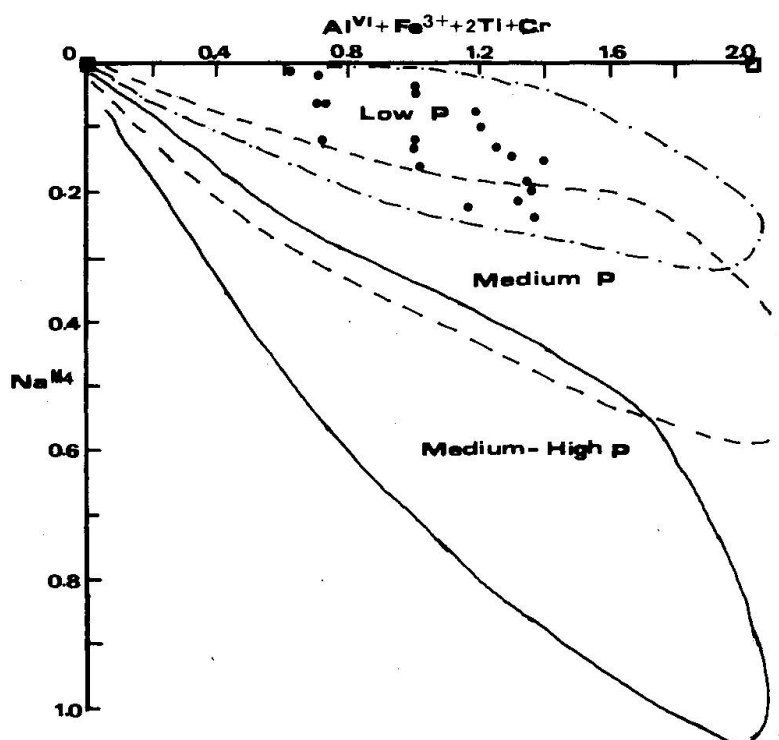


Fig. 3 Plot of amphiboles in study in LAIRD's et al. (1984) formula proportion variation diagram.

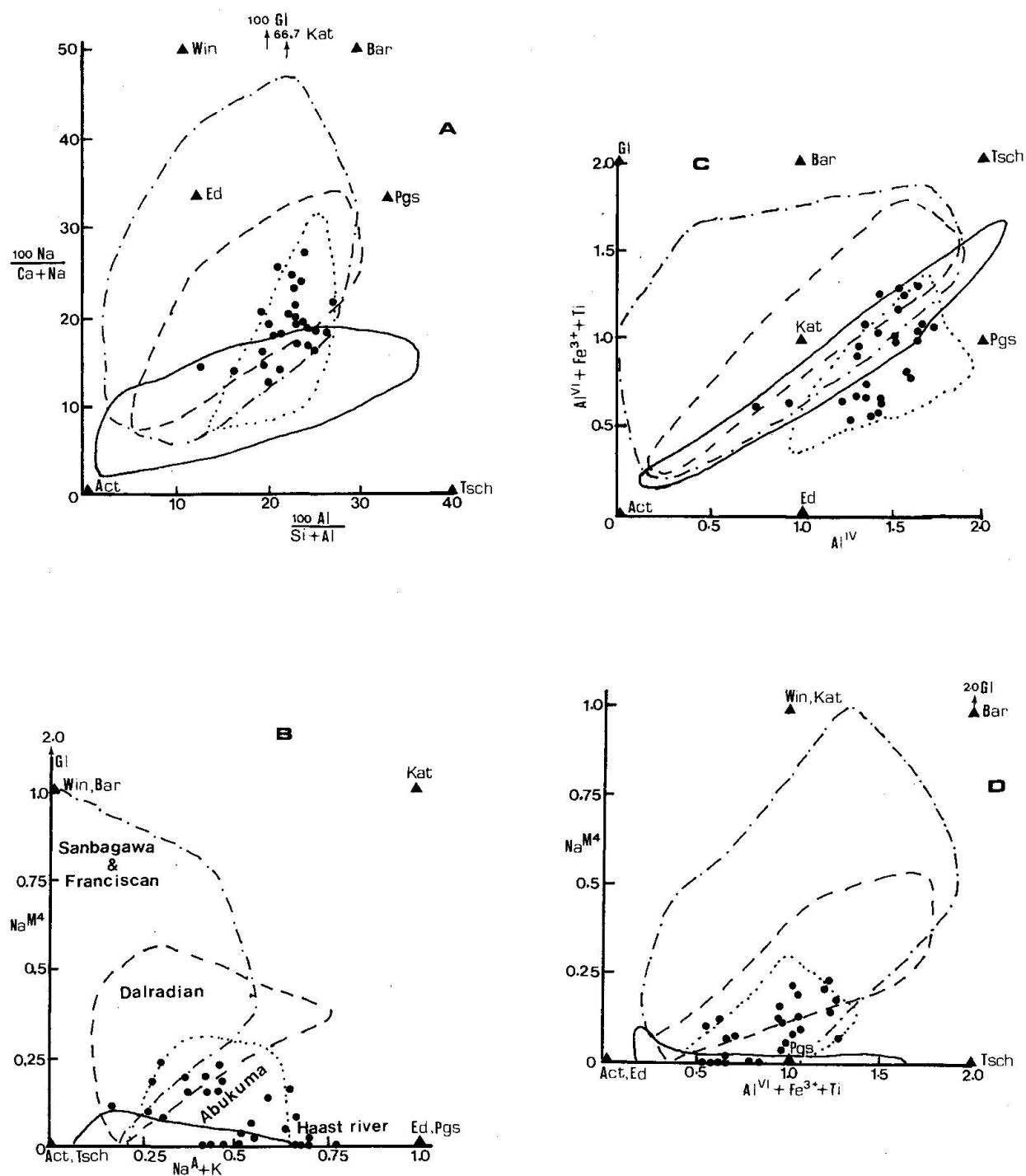


Fig. 4 Formula proportion diagrams (after LAIRD and ALBEE, 1981) for calcic and sodic-calcic amphiboles from various world-wide occurrences of mafic schist; that is, the high-pressure facies series Sanbagawa terrane in Japan, the high-pressure Franciscan terrane in California, the medium-pressure Dalradian terrane in south-western Scotland, the medium pressure Haast River Schist group in New Zealand and the low-pressure Abukuma terrane in Japan.

Act = actinolite, Bar = barroisite, Ed = edenite, Gl = glaucophane, Kat = katophorite, Pgs = pargasite, Tsch = tschermakite, and Win = winchite.

— Sanbagawa and Franciscan      ..... Abukuma  
 - - - - - Dalradian      — Haast river

MIYASHIRO, 1959), and between the amphibole end-members actinolite, edenite and pargasite.

Recent studies have proved that high pressure amphiboles from mafic rocks are richer in glaucophane than those of low pressure. In high-pressure facies metamorphism the glaucophane substitution  $[\text{Na}^{\text{M}}, (\text{Al}^{\text{VI}} + \text{Fe}^{3+} + \text{Ti} + \text{Cr}) \rightleftharpoons (\text{Fe}^{2+} + \text{Mg} + \text{Mn})]$  dominates, whereas the edenite  $[(\text{Na}^{\text{A}} + \text{K}), \text{Al}^{\text{IV}} \rightleftharpoons \square, \text{Si}]$  and tschermakite  $[(\text{Al}^{\text{VI}} + \text{Fe}^{3+} + \text{Ti} + \text{Cr}), \text{Al}^{\text{VI}} \rightleftharpoons (\text{Fe}^{2+} + \text{Mg} + \text{Mn}), \text{Si}]$  substitution dominate in low-pressure facies metamorphism. Besides, LEAKE (1965), RAASE (1974) and LAIRD and ALBEE (1981) have shown that low-pressure amphiboles are lower in  $\text{Al}^{\text{VI}}$  and higher in  $\text{Na}^{\text{A}}$ .

HYNES (1982) believes that the Ti content provides the best distinction between amphiboles from medium- and low-pressure, and he doubts the variation in Na,  $\text{Na}^{\text{M}}$ , Al or  $\text{Al}^{\text{VI}}$  as a function of pressure. A correlation of our amphiboles' Ti values versus total Al to Hyne's suggested discriminating diagram shows all samples exhibiting Ti/Al ratios of the low-pressure amphiboles.

Figure 4 A which is independent of data normalization shows the ordering of the fields in the same way as in the normalization dependent diagrams (Fig. 3 B, C and D) and the amphibole analyses plotting in the same field of low-pressure Abukuma terrane.

All the above show that is in fact a good correspondence between the amphibole composition and facies series and this correlation is not a consequence of normalization calculations.

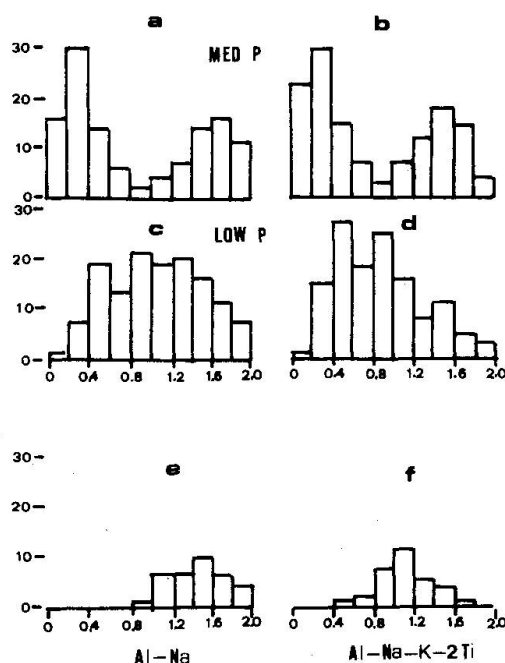


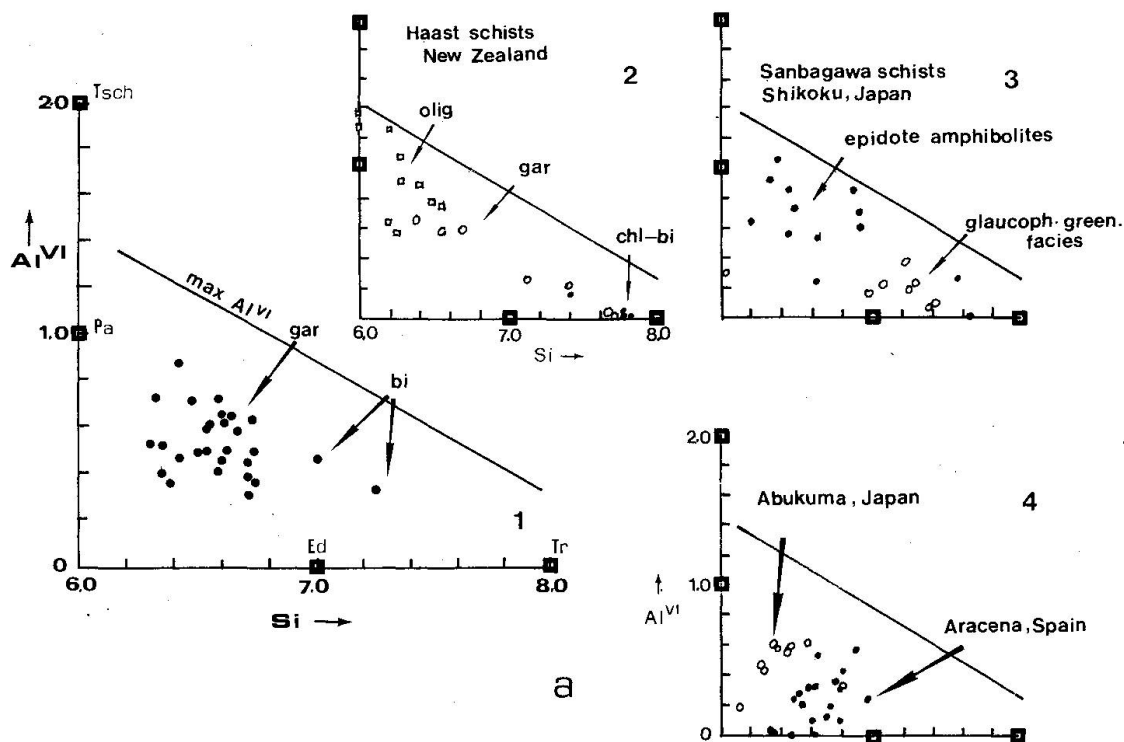
Fig. 5 Histograms of (Al-Na) and (Al-Na-K-2Ti) for medium- and low-pressure amphiboles. (a, b, c, d) after HYNES (1982) and our amphiboles (e, f). Data normalization to 23 oxygens with all iron as  $\text{Fe}^{2+}$ .



In Fig. 5 a, c and in relation to HYNÉ's 1982 proposed similar histograms, one can observe the range in (Al-Na), which is a measure of all Al in the amphibole other than that due to edenite- and glaucophane-substitution, supposing that all Na occurs in one of these types. Fig. 5 b, d presents the range in (Al-Na-K-2Ti) which is a measure of the tschermakite-component in the amphibole assuming that Ti is balanced by  $\text{Al}^{\text{VI}}$  substitution. All data were normalized to 23 oxygens with all iron considered as  $\text{Fe}^{2+}$ . It is obvious from Fig. 5 a, b that medium-pressure amphiboles show characteristically two broad peak areas, while the low-pressure ones appear with rather uniform distribution. Histograms e, f exhibit our amphiboles' distribution according to the same ranges (Al-Na) and (Al-Na-K-2Ti). Though the number of analyses is less than that of Hyne's we could say that the whole image shows a resemblance with sets c and d of the same figure, that is with Low-P samples.

#### COMPARISON WITH OTHER AREAS

In Fig. 6 a, b, c a comparison is made of the amphiboles' chemistry of this study with those from metabasites of other metamorphic terrains belonging to various facies series type. Plotting of Serbo-Macedonian amphiboles in 6a ( $\text{Al}^{\text{VI}}$  vs Si) shows them quite below the LEAKE's (1965) line of "maximum  $\text{Al}^{\text{VI}}$ " (Data normalized to 23 O with all iron as  $\text{Fe}^{2+}$ ). They occupy an area between the Abukuma and Aracena high-temperature, low-pressure metamorphic facies series type with the same Si range from 6.3 to 6.8 but a little higher  $\text{Al}^{\text{VI}}$  values.



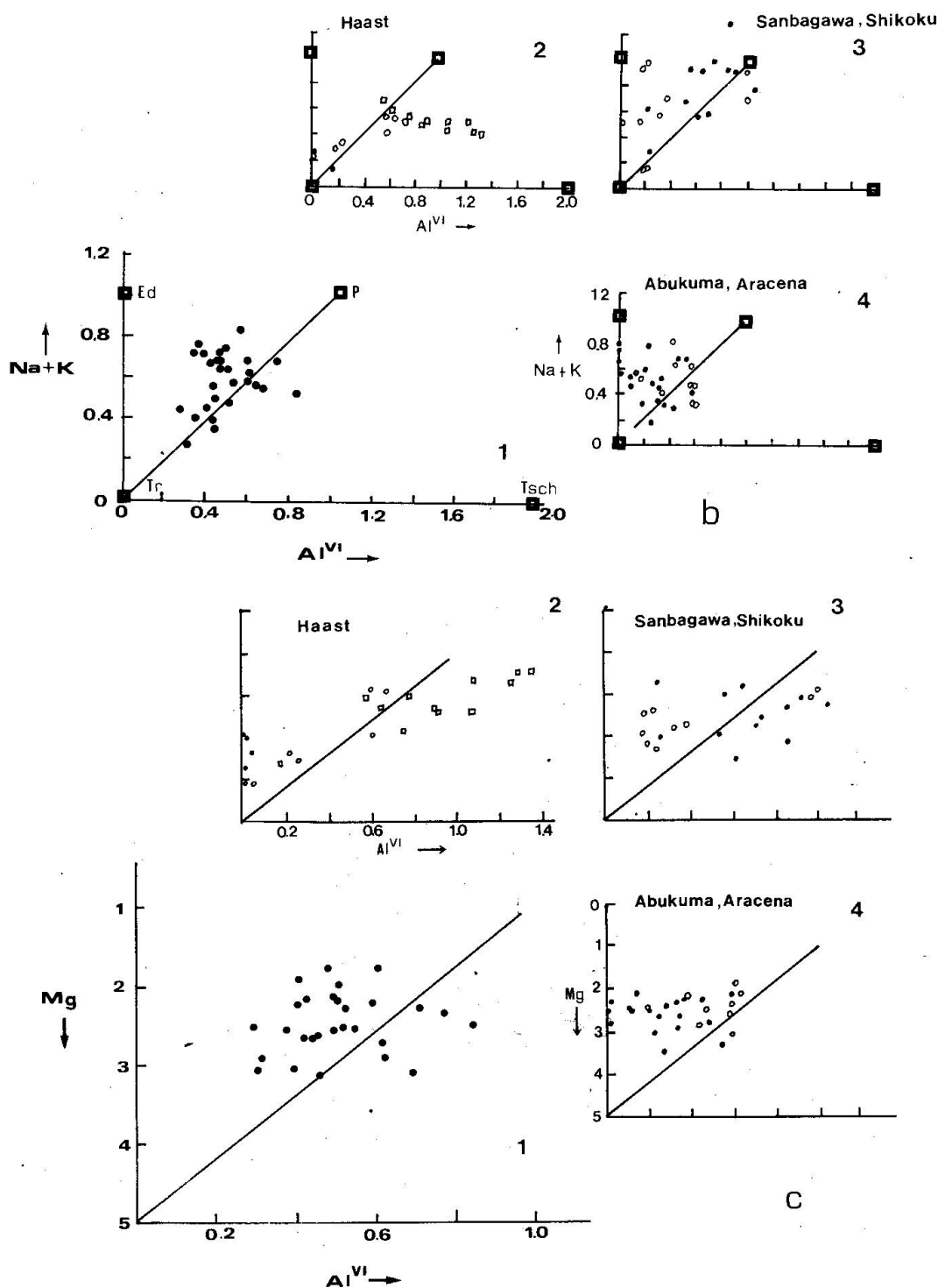


Fig. 6 Si vs  $\text{Al}^{\text{VI}}$ ,  $\text{Al}^{\text{VI}}$  vs  $(\text{Na} + \text{K})$  and  $\text{Al}^{\text{VI}}$  vs Mg for the studied amphiboles in comparison to relative diagrams from other areas. Tr = tremolite, Ed = edenite, Pa = pargasite, Tsch = tschermakite. 6a<sub>1</sub>, b<sub>1</sub>, c<sub>1</sub> = our amphiboles plotting. 6a<sub>2</sub>, b<sub>2</sub>, c<sub>2</sub> = Metabasite amphiboles of Haast Schists, New Zealand (COOPER and LOVERING, 1970); ● chlorite and biotite zones; ○ garnet zone; □ oligoclase zone. 6a<sub>3</sub>, b<sub>3</sub>, c<sub>3</sub> = Metabasite amphiboles of Sanbagawa Schists, Shikoku, Japan (BANNO, 1964); ● amphiboles of "epidote amphibolites" of higher-grade zones; ○ amphiboles of lower-grade "glaucophanitic" or greenschist facies zones. 6a<sub>4</sub>, b<sub>4</sub>, c<sub>4</sub> = Metabasite amphiboles of high-temperature, low-pressure metamorphic facies series terrains; ○ Abukuma, Japan (SHIDO, 1918); ● Aracena, SW Spain (BARD, 1970). Diagonal line represents line of maximum  $\text{Al}^{\text{VI}}$  for a given Si on the basis of 850 calciferous amphiboles after LEAKE (1965).

They also cover a part of the "epidote amphibolites" amphiboles of Shikoku and a part of garnet zone metabasite amphiboles of Haast schists. In Fig. 6b ( $\text{Na} + \text{K}$  vs  $\text{Al}^{\text{VI}}$ ) the Serbo-Macedonian massif amphiboles cover again the area between the Abukuma and Aracena metabasite amphiboles and a part of the "epidote amphibolites" calciferous amphiboles of Shikoku, between edenite and pargasite. Finally, in 6c ( $\text{Mg}$  vs  $\text{Al}^{\text{VI}}$ ) our amphiboles show a closer resemblance to the relative diagrams from literature plotting again between the Abukuma and Aracena plots.

#### THERMOBAROMETRIC EVALUATION OF METAMORPHISM

All the amphibolitic samples examined in this work are characterized by the coexistence of plagioclase and hornblende; this assemblage "typical" of the amphibolite facies exists over a wide range of temperatures, pressures and oxygen fugacity at  $P_{\text{H}_2\text{O}} = P_f$ .

The appearance of clinopyroxene coexisting with amphibole characterizes the upper limit of this assemblage. The beginning of the breakdown of hornblende to form clinopyroxene is experimentally determined for olivine tholeiite composition at temperatures as high as  $730^\circ \pm 12^\circ \text{C}$  to  $788^\circ \pm 8^\circ \text{C}$  at  $P_f$  from 0.5 to 2 Kbs, respectively (SPEAR, 1981b). The lower limit of the plagioclase hornblende assemblages is experimentally found for basaltic compositions at temperatures up to  $550^\circ \text{C}$ ,  $P_{\text{H}_2\text{O}} = 3 \text{ Kbs}$ , QFM buffer (LIOU et al., 1974).

On the assumption that the chemistry of hornblendes is considered to be influenced by the pressure of metamorphism and according to the previously mentioned diagrams, our amphiboles in study suggest T/P ratios at least high as for the Abukuma type metamorphism.

Following the experimental plagioclase-hornblende geothermobarometer drawn by PLYUSHINA (1982) our amphibole samples plot according to their Al content in the area between the isobars 2 and 4 Kbars. Things are more difficult with temperature estimation since for each isobar (2 and 4 Kb) the range of temperature is wide (nearly  $550^\circ$ – $650^\circ \text{C}$  according to Plyushina's experimental data).

In Fig. 7 the available pl-am pairs of the Serbo-Macedonian amphibolites give T values nearly between  $600^\circ \text{C}$  and  $630^\circ \text{C}$ . Two samples that escape contain biotite in their paragenesis.

#### DISCUSSION AND CONCLUSION REMARKS

Field observation as well as petrologic and isotopic studies have already shown that the Serbo-Macedonian formations have suffered several metamorphic events (KAUFMANN et al., 1976; KOCKEL et al., 1977; PAPADOPOULOS, 1982;

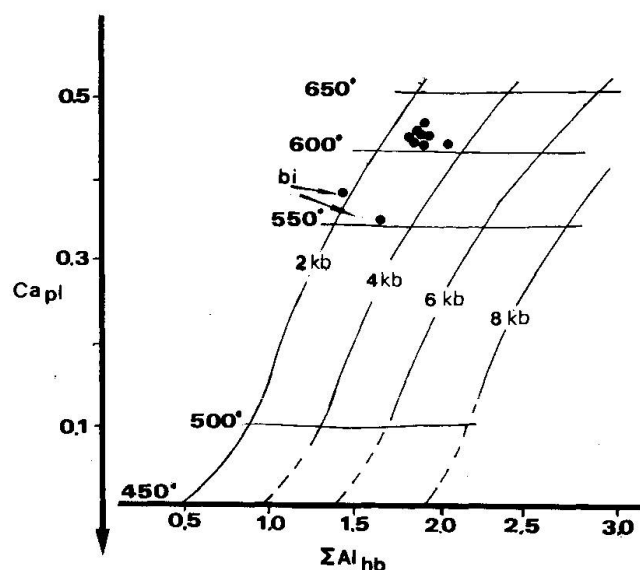


Fig. 7 An-content in pl vs  $\Sigma Al$  in hb as a function of P. T. conditions (after PLYUSHINA, 1982).

DIXON and DIMITRIADIS [in press]). This fact complicates geochemical research processes and final conclusions. Considering the amphibolite occurrences of the massif we have resulted, that the above rocks are products of regional metamorphism and of igneous origin. The mineral assemblages and composition confirm an amphibolite facies within the limits of which a slight increase of the P. T. conditions is deduced for the south-east areas of the zone. This results from the more calcic composition of plagioclases, their larger grain size, and greater proportion of pericline twins, in the samples of these areas. Besides, the appearance of diopside in these south-east places is characteristic (see also KASSOLI-FOURNARAKI, 1981). In no case the metamorphism proceeded up to the granulite facies since the paragenesis calcite-anorthite or hypersthene seem to be completely absent.

The consideration of the amphibole's chemistry in the present study, revealed some further-more elements for the P. T. conditions of metamorphism of these amphibolitic rocks.

Plotting of amphibole formula variations in relative discriminant diagrams shows in all cases the rock samples to possess mostly the area of garnet zone and a part of the upper biotite zone. In no case they reach the staurolite-kyanite zone. They also plot always in low-P fields resembling closer to the Abukuma low-pressure high-temperature metamorphic facies type.

As it is deduced the P conditions must be between 2 and 4 Kb. The temperature estimation proves more difficulties. The range between 600° C and 630° C according to PLYUSHINA (1982) experimental diagram seems a little low. Actually, we believe that at least the lower limit for temperature must not be below

the 650° C, and the upper limit at least for the south-eastern localities (where clinopyroxene appears in coexistence with amphibole) must not exceed the 740° C. Mainly, we base our assumption to the anorthite content of the plagioclases (basic oligoclase and andesine). FRISCH (1984), for a low-grade amphibolite consisting of plagioclase, 0–6% An, and amphibole (actinolite to magnesiohornblende), gives a T value of nearly 500° C. So, it proves that the much more calcic plagioclases of Serbo-Macedonian amphibolites justify higher temperatures. Besides, WINKLER (1979) refers that calcic oligoclase and andesine require temperatures much higher than 500° C.

Our suggestion is strengthened by Dixon and Dimitriadis (in press) who working on a part of the Serbo-Macedonian massif, the Volvi complex, analysed hornblende-garnet pairs in representative rocks of the district using a recently calibrated Mg/Fe<sup>2+</sup> exchange thermometer. The T results for a coronitic metagabbro and a fine-grained amphibolite were 720° and 753° C, correspondingly.

In summary, discriminant diagrams, mainly on the amphibole's chemistry, mineralogical assemblages, other minerals' composition as well as comparison to other rocks of the massif, construct a probable range of P 2–4 Kb and T 650°–740° C for the metamorphic conditions of the rocks in study.

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