

CHEMISTRY AND GEOCHEMISTRY OF SOME COEXISTING Ca - AMPHIBOLES AND Mg - BIOTITES *

BY

Dr. CONSTANTINE SIDERIS **

I. INTRODUCTION

The object of writing this paper is to demonstrate the distribution of the major and trace elements between the coexisting biotites and hornblendes separated from dacites and rhyodacites. These two minerals are the only ferromagnesian silicate minerals existing in their host volcanic rocks from West Thrace.

The geology and petrography of the above mentioned volcanic rocks have been described by GEORGALAS (1925), LIATSIKAS (1938) and RENTZEPERIS (1956).

The laboratory work was carried out at the Department of Mineralogy and Petrology, University of Cambridge, and the Institute of Mineralogy and Petrology, University of Athens.

II. METHODS OF CHEMICAL ANALYSES

(i) Major elements

The chemical analyses of the separated ferromagnesian minerals were essentially based on the system of WASHINGTON, but TiO_2 and MnO were determined colorimetrically, Na_2O and K_2O by flame photometry and total water by the Penfield tube method. The method of HUANG and JOHNS (1967) was used for the determination of the Fluorine in the biotites.

(ii) Trace elements

The determinations of the trace elements were carried out by Mr. R. S. Allen with the use of a Hilger - Watts spectrometer. The lines used and the sensitivity for each element are published in NOCKOLDS and ALLEN (1953).

* ΚΩΝ. ΣΙΑΡΕΡΗ. — Χημισμός και Γεωχημεία συνυπαρχόντων τινών Ca - Αμφιβόλων και Mg - Βιοτιτών.

** Address of the author :
Dr. C. G. SIDERIS University of Athens, Institute of Mineralogy and Petrology.

III. BIOTITES

Data of biotite chemical analyses are presented in the Table 1.

The structural formulae (Table 2) have been calculated on the basis of 24 (O, OH, F) assuming the formula $X_2Y_6Z_8O_{20}(OH, F)_4$ where $X=K, Na, Ca$ but also Ba, Rb, Cs , etc; $Y=Mg, Fe^{2+}, Fe^{3+}, Al, Ti$ and $Z=Si_{6-5}Al_{2-3}$ but perhaps Fe^{3+} or Ti . Thus the general structure of a

T A B L E 1
Biotite Analyses

	L71Bi	L52Bi	F20Bi	F25Bi	F55Bi
SiO ₂	37.75	38.91	37.84	37.76	37.69
TiO ₂	3.41	3.41	3.57	3.51	3.45
Al ₂ O ₃	15.33	15.30	15.35	15.54	15.74
Fe ₂ O ₃	4.72	4.13	5.09	4.31	3.53
FeO	10.40	9.42	9.74	10.13	10.52
MnO	0.23	0.18	0.25	0.18	0.11
MgO	14.53	15.79	15.31	15.64	15.97
CaO	0.62	0.82	0.32	0.35	0.38
Na ₂ O	0.76	0.72	0.71	0.76	0.82
K ₂ O	7.98	7.44	8.37	8.33	8.29
OH ₂ ⁺	3.77	3.85	3.31	3.30	3.30
OH ₂ ⁻	0.14	0.06	0.00	0.03	0.06
F ₂	<u>0.16</u>	<u>0.15</u>	<u>0.27</u>	<u>0.25</u>	<u>0.23</u>
	99.66	100.12	100.13	100.06	100.03
O≡F	0.06	0.06	0.11	0.10	0.09
Total	99.60	100.06	100.02	99.96	99.94

Analyst: Constantine Sideris

mica is a composite sheet in which a layer of six-fold coordinated cations (Y positions) is placed between two layers of linked tetrahedra made by (Si, Al)O₄ in which the cations are four-fold coordinated (Z positions). Large interlayer cations are lying between them in twelve-fold coordination (X positions) (DEER - HOWIE - ZUSSMAN, (1967).

The possible variations in the compositions of biotites and phlogopites and their relations to muscovites are shown in the Fig. 1 (ibidem). The chemical variations of the analyzed biotites expressed as the number of the six-fold coordinated trivalent ions and the number of Si ions are plotted within the double dashed area. Also the ratio 100 Mg:

(Mg + Fe + Ti + Mn) and the summations of the positive and negative charges are given in the Table 2. The participation of the major and trace elements are given in the Table 3. In Fig. 2 the phlogopite-biotite compositional fields are shown (after DEER-HOWIE-ZUSSMAN, 1967).

The chemical variations of the analyzed biotites are plotted within the dashed area. The fair but definite superiority in the participation

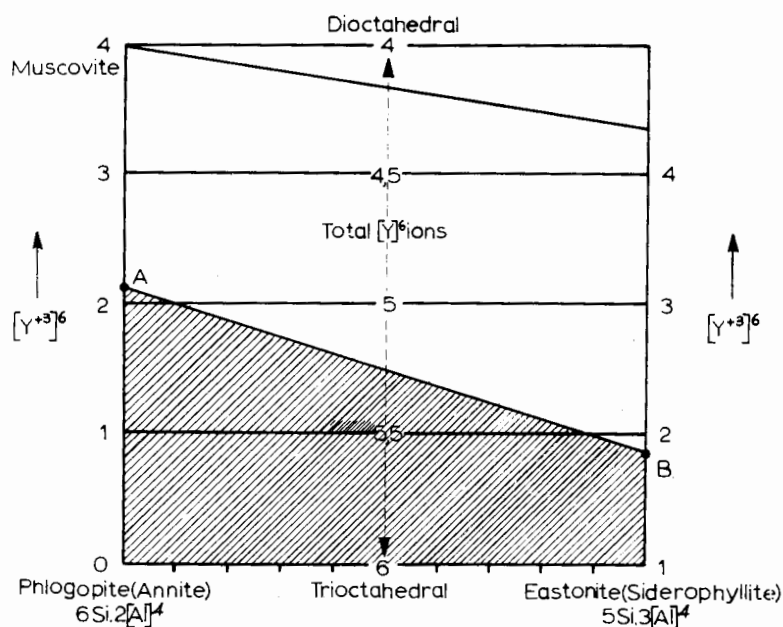


Fig. 1. Possible variations in the compositions of phlogopites and biotites and their relations to the composition of muscovites after Deer, Howie, and Zussman (1967). Analyzed biotites plot within the double dashed area.

of Mg against its substitutes in the octahedral sites and the substitution of the Si by the Al about the ratio 5.5:2.5 in tetrahedral are shown in this Fig.

The interpretation of the variations in the chemical composition of analyzed specimens is shown in the followed diagrams in which the total number of ions in the group Y is used as abscissa. The tetrahedrally coordinated Z group of elements consists entirely of Si and Al; presumably all the sites are occupied. Fig. 3 and 4 shows the variations of the analyzed biotites expressed as the number of ions of each element in four- and six-fold coordination, respectively, and the total number of

ions in the Y group. Si falls and Al_{iv} rises with increasing number of cations in group Y. Also, Ti and Al_{vi} rise fairly, Mg rises strongly but the summation (Fe³⁺ + Fe²⁺) falls in the same direction. It is obvious that the Mg is replaced by Fe mainly (DEER - HOWIE - ZUSSMAN, 1967).

T A B L E 2

Structural formulae of biotites, recalculated to 24 (O, OH, F).

	L71Bi	L52Bi	F20Bi	F25Bi	F55Bi
Si	5.574	5.652	5.595	5.579	5.558
Al	2.426	2.348	2.405	2.421	2.442
Al	.236	.272	.259	.280	.288
Ti	.372	.366	.390	.382	.381
Fe ³⁺	.514	.436	.550	.462	.390
Fe ²⁺	1.278	1.144	1.199	1.252	1.294
Mn	.026	.017	.026	.017	.008
Mg	3.195	3.415	3.366	3.438	3.510
Ca	.097	.122	.044	.053	.053
Na	.213	.192	.195	.213	.230
K	1.491	1.362	1.563	1.563	1.560
O	20.220	20.210	20.626	20.643	20.650
OH	3.709	3.721	3.250	3.251	3.244
F	.071	.069	.124	.106	.106
Z	8.000	8.000	8.000	8.000	8.000
Y	5.621	5.650	5.781	5.831	5.871
X	1.801	1.676	1.802	1.829	1.841
OH+F	3.780	3.790	3.374	3.357	3.350
$\frac{\text{Mg}}{\text{Mg}+\text{Fe}+\text{Mn}}$	63.7	68.1	65.4	66.5	67.4
Positive charges	44.20	44.19	44.61	44.62	44.63
Negative charges	44.22	44.21	44.62	44.64	44.65

The number of Si ions in the Z group is slightly higher and the number of Al ions in the Y group greatly higher than the ones mentioned by NOCKOLDS (1947) for biotites associated with hornblendes (average values of 18 analyses; 5.53 Si ions in the Z group and 0.15 Al ions in the Y group), but these biotites are belonging to holocrystalline rocks, except

T A B L E 3
Participation of elements in biotites (ppm)

	L71Bi	L52Bi	F20Bi	F25Bi	F55Bi
Si	184.32 x 10 ³	189.92 x 10 ³	183.20 x 10 ³	182.87 x 10 ³	182.25 x 10 ³
Al	84.72 x 10 ³	84.20 x 10 ³	84.09 x 10 ³	85.20 x 10 ³	86.31 x 10 ³
Ti	21.34 x 10 ³	21.22 x 10 ³	22.12 x 10 ³	21.76 x 10 ³	21.40 x 10 ³
Fe ³⁺	34.48 x 10 ³	30.00 x 10 ³	36.86 x 10 ³	31.19 x 10 ³	25.52 x 10 ³
Fe ²⁺	84.41 x 10 ³	76.17 x 10 ³	77.73 x 10 ³	81.53 x 10 ³	84.72 x 10 ³
Mn	1.85 x 10 ³	1.39 x 10 ³	1.93 x 10 ³	1.39 x 10 ³	.85 x 10 ³
Mg	91.50 x 10 ³	99.04 x 10 ³	95.60 x 10 ³	97.71 x 10 ³	99.76 x 10 ³
Ca	4.57 x 10 ³	6.07 x 10 ³	2.35 x 10 ³	2.57 x 10 ³	2.78 x 10 ³
Na	5.86 x 10 ³	5.48 x 10 ³	5.41 x 10 ³	5.78 x 10 ³	6.23 x 10 ³
K	69.15 x 10 ³	64.25 x 10 ³	71.89 x 10 ³	71.64 x 10 ³	71.30 x 10 ³
Cr	27	17	32	27	32
Sc	-	-	-	-	-
La	-	-	-	-	-
Co	36	60	75	75	75
Zr	-	-	-	-	-
Ni	28	36	36	28	45
Y	-	-	-	-	-
Cu	21	28	24	21	24
V	270	270	320	320	420
Ga	20	30	25	20	30
Sn	-	-	-	-	-
Pb	-	-	-	-	-
Ba	3500	3500	3500	3500	3500
Sr	12	10	-	10	-
Rb	1000	180	140	180	180
Li	60	32	25	32	25
Cs	-	-	-	-	-

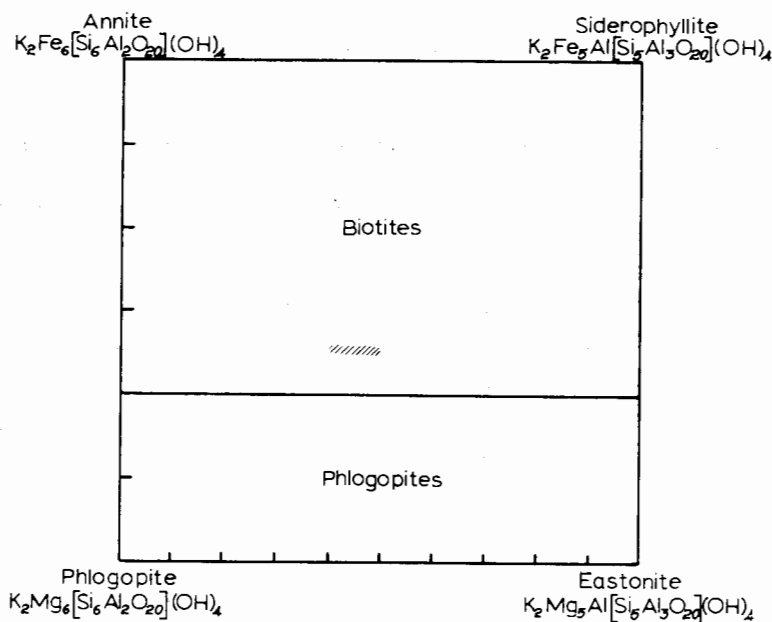


Fig. 2. Phlogopite-biotite compositional field after Deer, Howie, and Zussman (1967). Analyzed biotites plot within the dashed area.

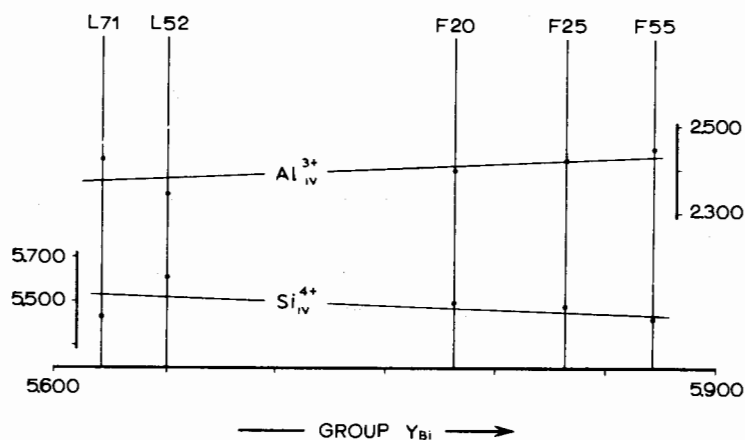


Fig. 3. Chemical variations of analyzed biotites expressed as the number of Si and Al ions in 4-fold coordination and the total number of ions in Y-group.

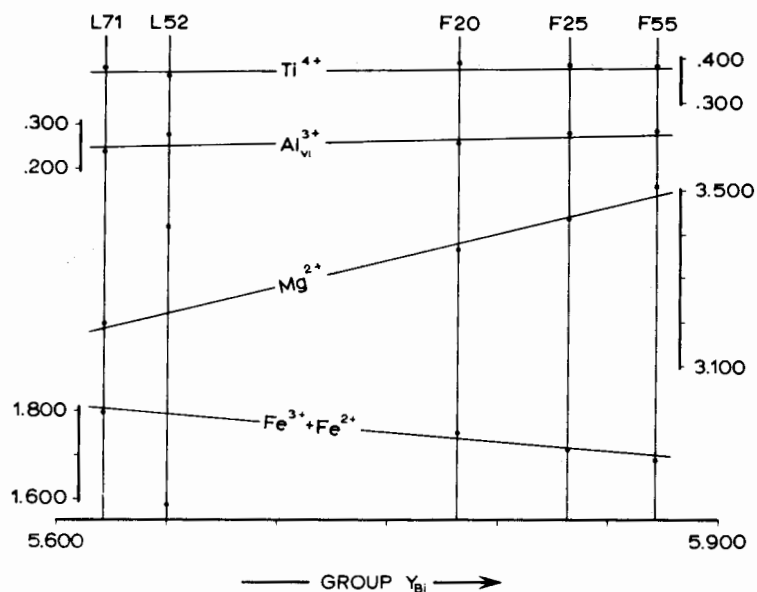


Fig. 4. Chemical variations of analyzed biotites expressed as the number of ions in 6-fold coordination and the total number of ions in Y-group.

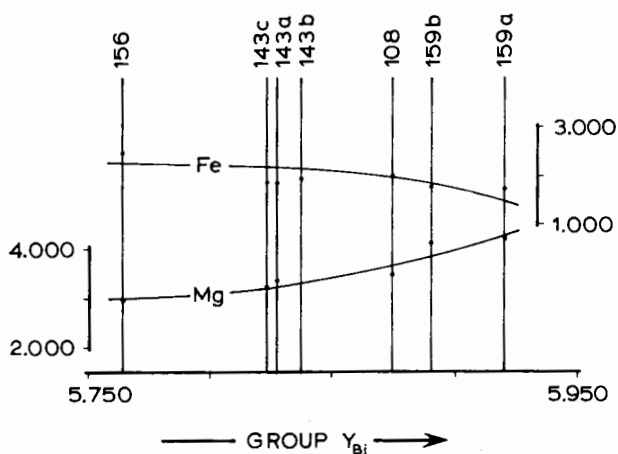


Fig. 5. Chemical variations of biotites from island Cos, Greece, expressed as the number of Fe- and Mg-ions in 6-fold coordination and the total number of ions in Y-group.

one. The increased concentration of the Mg covering the elimination of the Fe is mainly responsible for the total increase of the number of the six-fold coordinated ions. The same variations between the number of the Fe and Mg ions in biotites of volcanic rocks from the islands Cos

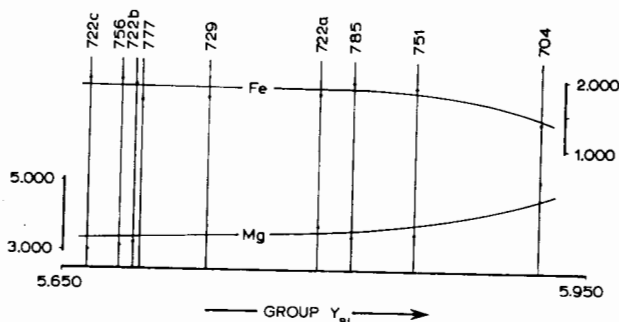


Fig. 6. Chemical variations of biotites from island Patmos, Greece, expressed as the number of Fe- and Mg-ions in 6-fold coordination and the total number of ions in Y-group.

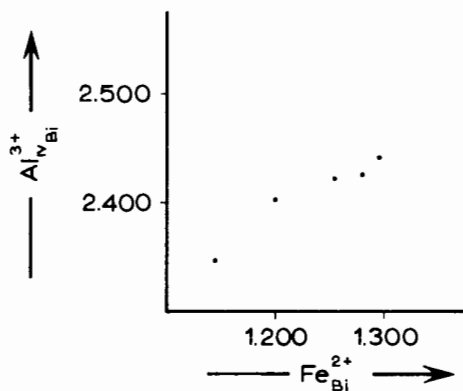


Fig. 7. Chemical variations of analyzed biotites expressed as the number of Al-ions in 4-fold coordination and the number of Fe²⁺-ions in 6-fold coordination.

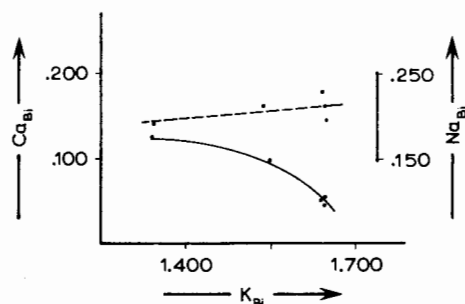


Fig. 8. Chemical variations of analyzed biotites expressed as the number of Ca-ions and Na-ions v. the number of K-ions.

and Patmos, Dodecanese, Greece (PECKETT, 1969) are shown in Fig. 5 and 6. The substitution of the quadrivalent Si by the trivalent Al in tetrahedral sites results to a decrease of the positive charges in the Z group. This substitution may be mainly balanced by an increase of the total number of six-fold coordinated ions. There is not observed an increase of the trivalent and quardivalent ions in the Y group; on the

contrary, a strange negative correlation between the rise of the Al_{iv} and the number of the ions mentioned above is observed in the specimens F55, F25, L71, and L52. There only rises Fe^{2+} with the increasing values of Al_{iv} , as shown in Fig. 7. It is interesting to interpret into the data of the biotites L52 and L71 in which the summation of the

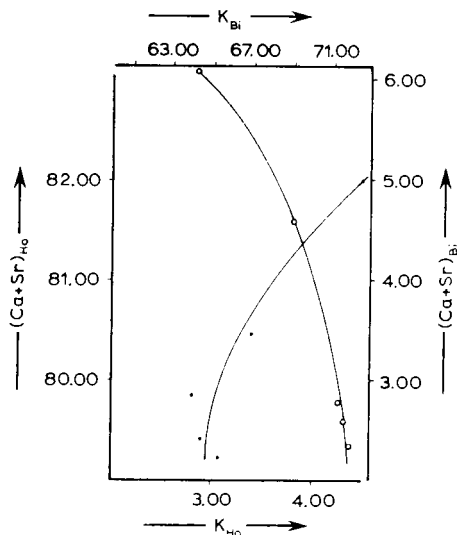


Fig. 9. Chemical variations of analyzed biotites and hornblendes expressed as the participation of $(Ca+Sr)$ -ions v. K-ions.

positive charges in Y group is lower than in the other specimens. Thus in these specimens a decrease of the ratio O/OH , F and an increase of the participation of the bivalent Ca are observed, in comparison with the other three specimens. A definite negative correlation between the number of Ca ions and the K ions is observed in the Fig. 8. (see also correlation between the $Ca+Sr$ v. the K in Fig. 9).

The separated grains of biotites have been tested very carefully in order to avoid impurities. In the same Fig. 8 there are shown the slight variations of the Na with the increasing values of the participation of K. At last the ratio $Ca+Sr/K$ increases in relation with the ratio Mg/Fe and the summation of the alkali earths rises towards the more Mg-rich biotites (from the Table 3) (see also PANKHURST, 1968).

IV. HORNBLENDENES

Data of the chemical analyses are presented in the Table 4. The high content of Ca in the analyzed specimens is obvious. The structural

formulae (Table 5) have been calculated on the basis of 24 (O, OH) assuming the formula $AX_3Y_3Z_3O_{22}(OH)_2$, where $X = Ca, Na, K$; $Y = Mg, Fe^{2+}, Fe^{3+}, Al, Ti, Mn$ and $Z = Si, Al$. Thus the structure contains talk-like strips made up by five cations in the sites M_1 , M_2 and M_3 (Y positions in

T A B L E 4
Hornblende Analyses

	L71Ho	L52Ho	F20Ho	F25Ho	F55Ho
SiO ₂	45.02	46.24	46.98	47.42	47.87
TiO ₂	1.53	1.48	1.32	1.16	1.01
Al ₂ O ₃	10.59	9.74	8.68	8.66	8.65
Fe ₂ O ₃	4.47	4.15	4.42	3.63	2.84
FeO	8.40	8.58	8.54	9.18	9.83
MnO	.41	.49	.43	.48	.54
MgO	14.50	14.99	15.26	15.16	15.06
CaO	11.26	11.09	11.87	10.93	11.00
Na ₂ O	1.51	1.35	1.15	1.36	1.31
K ₂ O	.54	.41	.37	.35	.34
OH ₂ ⁺	1.53	1.49	1.50	1.39	1.37
OH ₂ ⁻	.05	.04	.06	.06	.06

Total	99.81	100.04	99.58	99.78	99.88

Analyst: Constantine Sideris

six-fold coordination) placed between two bands of tetrahedra (Z positions in four-fold coordination). The larger cations are occupying the M_1 sites (X positions between six- and eight-fold coordination) and in some cases the A positions (approximately in ten-fold coordination). The latter ones are occupied by alkali only when more than 2 (Ca, Na, K) ions are present at the M_1 sites which are preferentially occupied by Ca (DEER - HOWIE - ZUSSMAN, 1967). Only Na but probably not K may replace Ca in the A position (PHILLIPS, 1963). As it is in general accepted the A position-cations are incorporated to the X-position-cations in the given structural formulae. Thus any excess of alkali ions above that one corresponding to the completion of 2.000 ions of X position must be regarded as the number of alkali ions in A position. The ratio 100 Mg: (Mg + Fe + Ti + Mn) and the summation of the positive and the negative charges are given in the same Table. The participation of the major and the

trace elements is given in the Table 6. The chemical variations of the analyzed hornblendes expressed as the numbers of $(Al_{iv} + Fe^{3+} + Ti)$

T A B L E 5

Structural formulae of hornblendes, recalculated to 24 (O, OH)

	L71Ho	L52Ho	F20Ho	F25Ho	F55Ho
Si	6.610	6.750	6.871	6.943	6.998
Al	1.390	1.250	1.129	1.057	1.002
Al	.428	.417	.364	.421	.473
Ti	.167	.158	.140	.123	.105
Fe ³⁺	.476	.438	.474	.387	.298
Fe ²⁺	1.023	1.044	1.036	1.117	1.194
Mn	.044	.052	.052	.052	.061
Mg	3.168	3.256	3.321	3.300	3.275
Ca	1.763	1.729	1.695	1.707	1.721
Na	.423	.368	.316	.369	.368
K	.088	.070	.052	.052	.052
O	22.518	22.561	22.542	22.645	22.666
OH	1.482	1.439	1.458	1.355	1.334
Z	8.000	8.000	8.000	8.000	8.000
Y	5.306	5.365	5.387	5.400	5.406
X	2.274	2.167	2.063	2.168	2.141
OH	1.482	1.439	1.458	1.355	1.334
Mg					
Mg-Fe-Mn	67.2	67.9	68.0	67.9	67.8
Positive charges	46.49	46.54	46.52	46.63	46.65
Negative charges	46.51	46.56	46.54	46.64	46.66

and Al_{iv} atoms per formula unit are plotted within the dashed area of the Fig. 10 (after DEER - HOWIE - ZUSSMAN 1967).

The tetrahedrally coordinated Z group of elements entirely consists of Si and Al; presumably all the sites are occupied, as in the biotites. Figs 11 and 12 show the variations of the analyzed hornblendes, expressed as the number of ions of each element in four- and six-fold coordination, respectively, and the total number of ions in the group Y. There

T A B L E 6

Participation of elements in hornblendes (ppm)

	L71Ho	L52Ho	F20Ho	F25Ho	F55Ho
Si	214.24×10^3	219.38×10^3	224.01×10^3	226.34×10^3	227.28×10^3
Al	57.05×10^3	52.28×10^3	46.83×10^3	46.57×10^3	46.46×10^3
Ti	9.29×10^3	8.99×10^3	8.03×10^3	7.01×10^3	6.11×10^3
Fe ³⁺	31.84×10^3	29.44×10^3	31.47×10^3	25.80×10^3	20.14×10^3
Fe ²⁺	66.46×10^3	67.62×10^3	67.70×10^3	72.52×10^3	77.57×10^3
Mn	3.17×10^3	3.79×10^3	3.33×10^3	3.71×10^3	4.18×10^3
Mg	89.02×10^3	91.74×10^3	93.85×10^3	92.94×10^3	92.22×10^3
Ca	81.90×10^3	80.40×10^3	79.18×10^3	79.40×10^3	79.83×10^3
Na	11.35×10^3	10.16×10^3	8.67×10^3	10.23×10^3	9.86×10^3
K	4.48×10^3	3.40×10^3	3.07×10^3	2.90×10^3	2.82×10^3
Cr	100	22	45	45	27
Sc	200	125	200	200	125
La	-	-	-	-	-
Co	36	28	36	45	-
Zr	100	120	260	180	75
Ni	60	17	22	28	22
Y	170	170	220	220	100
Cu	36	24	45	45	18
V	270	220	220	270	320
Ga	15	15	15	15	15
Sn	-	-	-	-	-
Pb	-	-	-	-	-
Ba	100	45	680	260	18
Sr	100	65	65	15	24
Rb	-	-	-	-	-
Li	32	32	60	25	25
Cs	-	-	-	-	-

is observed also, a close correlation in substitutions of the Fe^{3+} , Al_{vi} , Mg, and Fe^{2+} though the value of $(\text{Fe}^{2+} + \text{Fe}^{3+})$ is constant. Ti shows a fall

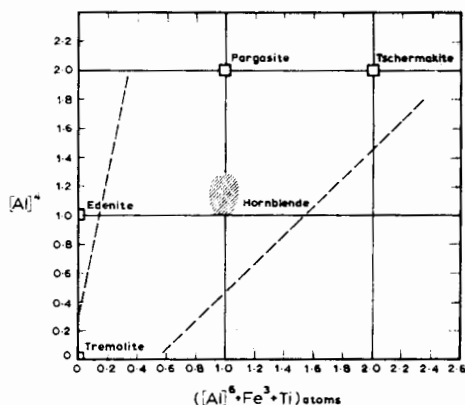


Fig. 10. The chemical variations of the calcium-rich amphiboles expressed as the numbers of $(\text{Al}_{\text{vi}} + \text{Fe}^{3+} + \text{Ti})$ and Al_{iv} atoms per formula unit after Deer, Howie, and Zussman (1967). Analyzed hornblendes plot within the dashed area.

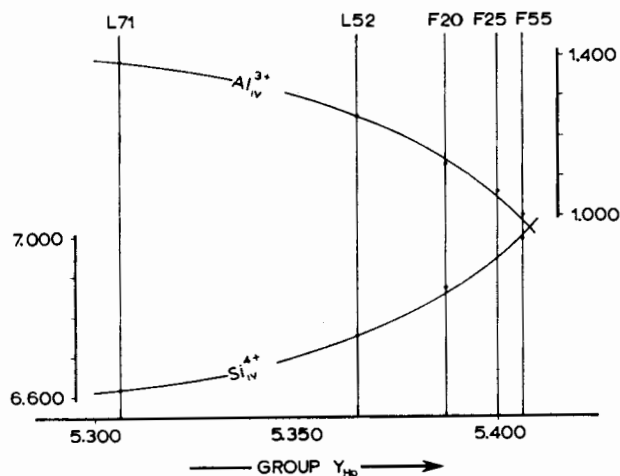


Fig. 11. Chemical variations of analyzed hornblendes expressed as the number of Si- and Al-ions in 4-fold coordination and the total number of ions in Y-group.

with the increasing values of group Y. In Fig. 13 there is shown a definite negative correlation between Ca and Mg. In Fig. 9 there is shown the correlation between $\text{Ca} + \text{Sr}$ v. the K. In general the number of the

cations in Y position is less than the same number in the case of the corresponding biotites. The same correlation is observed in recalculated analyses of coexisting biotites and hornblendes from the quartz diorites and granites at Ben-Nevis, Scotland (HASLAM, 1968) and from the volcanic rocks of Kefalos peninsula of Cos island, Dodecanese, Greece PECKETT, 1969).

The substitution of the quadrivalent Si by the trivalent Al in the tetrahedral sites results to a decrease of the positive charges in the Z

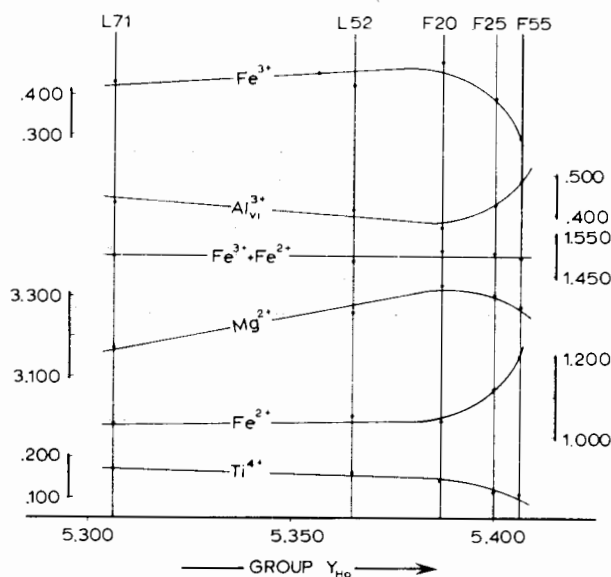


Fig. 12. Chemical variations of analyzed hornblendes expressed as the number of ions in 6-fold coordination and the total number of ions in Y-group.

group as it is observed in the case of biotites. This substitution must be mainly balanced by the increase of the number of the trivalent and quadrivalent ions in Y group and an increased entry of alkali in the A sites. Thus Fig. 14 shows the variations of the analyzed hornblendes expressed as the number of Al ions in tetrahedral sites and the summation of $(Al_{iv} + Ti + Fe^{3+})$ ions in Y group and shows also, how the Al_{iv} rises with the increasing values in the number of trivalent and quadrivalent ions in octahedrally coordinated sites. It must be underlined that in the analyzed hornblendes there is an excess of alkali ions and a partial occupation of the A sites might be assumed. The recalculated analyses give more than 5.000 ions in the Y position and would be possible that

charge deficits may be balanced also by this excess. The substitution of the Ca by alkali which is shown in Fig. 15 also results to a decrease

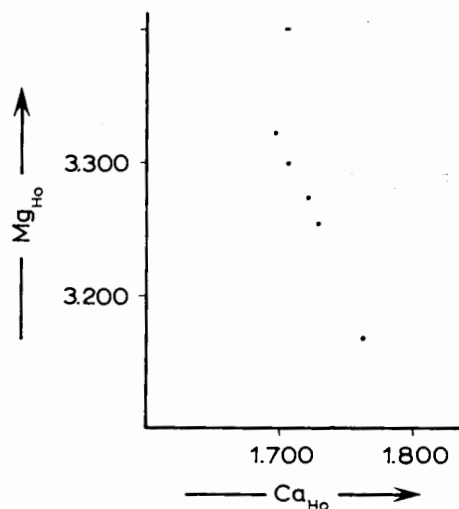


Fig. 13. Chemical variations of analyzed hornblendes expressed as the number of Mg-ions v. the number of Ca-ions.

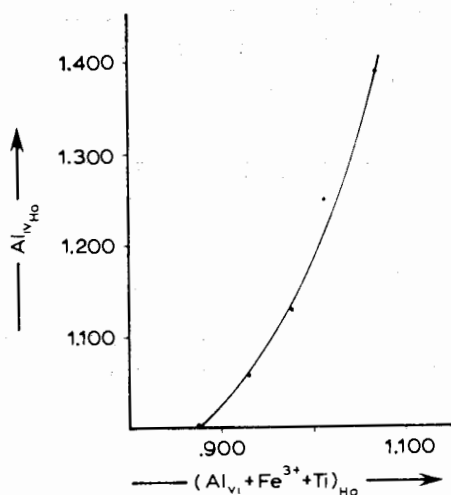


Fig. 14. Chemical variations of analyzed hornblendes expressed as the number of Al-ions in 4-fold coordination and the number of trivalent and quadrivalent ions in 6-fold coordination.

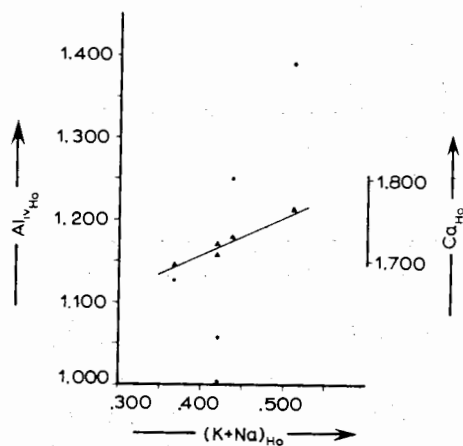


Fig. 15. Chemical variations of analyzed hornblendes expressed as the number of Al_{iv} -ions and Ca-ions v. the summation of (K+Na)-ions.

of positive charges. The charge deficit may be balanced, as in the case of $Si_{iv}^{4+} \leftarrow Al_{iv}^{3+}$ substitution. However, it is obvious that a corresponding

correlation between the alkali ions and the summation ($Al_{vi} + Ti + Fe^{3+}$) might be assumed. Moreover the variation of the number of the more than 2.000 ions in the A sites is not in linear correlation with any of the substitutions mentioned above and it would be possible that the charge deficits are preferentially balanced by charges of six-fold coordinated ions.

V. RELATIONS BETWEEN THE COEXISTING BIOTITES AND HORNBLENDES

The rise and the fall of the ratio $\frac{Si_{iv}^{4+}}{Al_{iv}^{3+}}$ with the increasing values in the total number of the six-fold coordinated ions in the hornblendes and biotites respectively results into the charge deficit mentioned above.

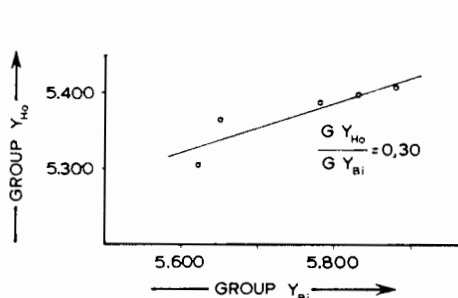


Fig. 16. The distribution of the total number of ions in Y-group between the analyzed ferromagnesian minerals.

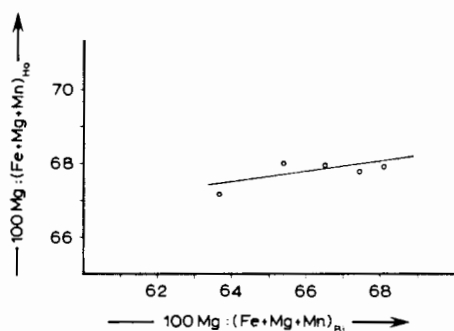


Fig. 17. The distribution of Mg between the analyzed ferromagnesian minerals.

In respect with the balance of this charge deficit it is interesting to deal with the distribution coefficient of the total number of ions in Y groups of the two coexisting minerals. Thus $\frac{GY_{Ho}}{GY_{Bi}}$ is equal to 0.30 (Fig. 16), which means that there is a great capacity in the biotites to undergo variations in the number of the six-fold coordinated ions, at least, in the specimens analyzed. Then in the biotites in which there exists the ability mentioned above and the ratio $\frac{Si_{iv}^{4+}}{Al_{iv}^{3+}}$ falls with the increasing values in the number of the six-fold coordinated ions, the charge deficit is mainly balanced by the increase of the total number of the octahedrally sited ions. On the other hand in the hornblendes in

which the ratio $\frac{\text{Si}_{iv}^{4+}}{\text{Al}_{iv}^{3+}}$ rises with fairly increasing values in the number of the six-fold coordinated ions, the charge deficit is balanced mainly by the increase of the trivalent and quadrivalent ions in the Y positions and the number of the alkali ions. Also, the linear positive correlation of the total number of ions in the Y groups of the two coexisting minerals, may indicate that the increase of the ions depends on the same cause of the particular conditions during the crystallization order of the different magmatic liquids.

The relation of the distribution of the Si in the two coexisting ferromagnesian minerals, as shown in Tables 3 and 6, suggests that in

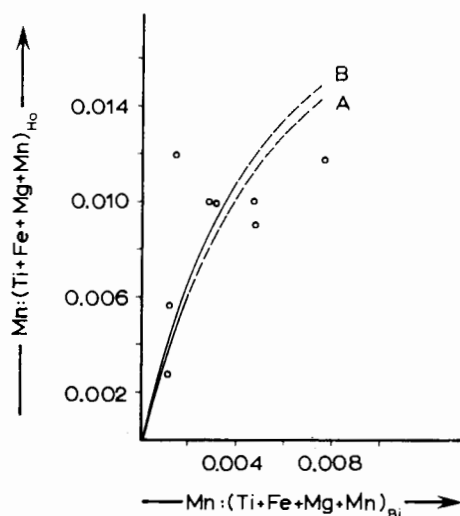


Fig. 18. The distribution of Mn between coexisting biotites and hornblendes (B=from volcanic rocks of Aegean sea, A = from gneisses of N. W. Quebec).

the biotites and the hornblendes of these volcanic rocks, equilibrium with respect to Si is unlikely to have been attained. Thus the difference between the maximum and the minimum number of the Si ions in Z positions is equal to 0.094 for the biotites and 0.388 for the hornblendes. A comparison of the Tables 3 and 6 shows also that the contribution of the elements Ti, Al, Fe and Mg is greater in the biotites than in the coexisting hornblendes. Similar relations in the distribution, but lower values in the biotites, are observed in the cases of the Al and Ti.

Thus the small variations of the contribution of the Al and the Ti in the biotites in comparison with the hornblendes and the lower values

of the Fe in the latter are shown in the same Tables. The distribution of the Mg in the coexisting ferromagnesian minerals is expressed by the usual ratio $100 \text{ Mg} : (\text{Fe} + \text{Mn} + \text{Mg})$ (Fig. 17). As shown, the substitution of the Mg extends to wider limits in the biotites than its associated hornblendes and a linear correlation of this substitution is observed between the coexisting minerals. The distribution of Mn is shown in Fig. 18 (curve B) in respect with the ratios $\text{Mn} : (\text{Ti} + \text{Fe} + \text{Mg} + \text{Mn})$ of the coexisting minerals from the volcanic rocks of W. Thrace and two other known cases from Kefalos peninsula of Cos island (PECKETT, 1969).

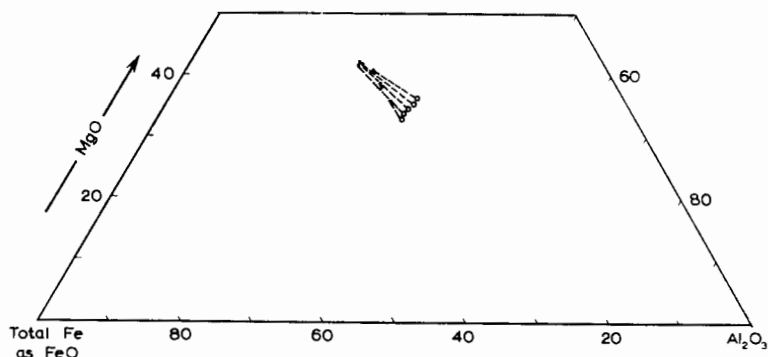


Fig. 19. Ternary variation diagram showing relation between the contents of MgO, total Fe as FeO, and Al_2O_3 in the analyzed ferromagnesian minerals (small dots represent biotites).

In the same Fig. 18 the distribution of the Mn between the coexisting biotites and hornblendes from the gneisses of N. W. Quebec is represented by the curve A (after KRETZ, 1959). The distribution of this element between biotites and hornblendes obeys Nernst's law at low concentrations but shows a departure at higher concentrations which may indicate that the equilibrium was not completely established (DEER - HOWIE - ZUSSMAN, 1967). It is very interesting to observe the similarity of the distribution of the Mn between the coexisting minerals though either the host rocks or the conditions of the crystallization are so different. Fig. 19 shows the distribution of the total Fe as FeO, MgO, and Al_2O_3 . The general direction of the tie lines connecting the hornblendes and the biotites proves that the ratio $\text{FeO}_T : (\text{FeO}_T + \text{MgO} + \text{Al}_2\text{O}_3)$ decreases in the biotites. Small variations of the Na in the biotites and the K in the hornblendes are shown in Tables 3 and 6. Also, the biotites L52 and L71, in which a high proportion of Ca has been determined, are coexisting with hornblendes in which the higher proportion of this element has been observed among the analyzed specimens. In Fig. 9 there is shown an opposite correlation between biotites and hornblendes in the variations of the summation $(\text{Ca} + \text{Sr})$ v. K.

VI. CHEMICAL RELATIONS BETWEEN THE FERROMAGNESIAN MINERALS AND THEIR HOST ROCKS

The data of the chemical analyses of the volcanic host rocks and the participation of the elements in ppm are given in Tables 7 and 8

T A B L E 7
Host volcanic rocks Analyses

	L71	L52	F20	F25	F55
SiO ₂	61.81	66.20	67.94	64.46	60.59
TiO ₂	.57	.40	.53	.56	.59
Al ₂ O ₃	17.38	15.52	16.04	16.56	17.48
Fe ₂ O ₃	2.99	2.04	.55	1.67	2.83
FeO	1.12	1.71	1.04	1.52	1.97
MnO	.04	.05	.04	.06	.08
MgO	2.21	1.88	1.55	2.02	2.69
CaO	4.08	4.63	4.42	4.60	4.58
Na ₂ O	3.09	3.17	2.96	2.95	2.98
K ₂ O	3.36	2.35	2.33	2.44	2.52
P ₂ O ₅	.14	.15	.12	.12	.12
OH ₂ ⁺	1.64	1.23	1.09	1.85	2.66
OH ₂ ⁻	1.67	.67	1.19	1.12	1.02
Total	100.10	100.00	99.80	99.93	100.11

T A B L E 8
Participation of elements in host volcanic rocks Analyses

	L71	L52	F20	F25	F55
Si	298.47 x 10 ³	315.44 x 10 ³	325.65 x 10 ³	310.77 x 10 ³	293.71 x 10 ³
Ti	3.47 x 10 ³	2.39 x 10 ³	3.23 x 10 ³	3.41 x 10 ³	3.65 x 10 ³
Al	94.99 x 10 ³	83.72 x 10 ³	87.00 x 10 ³	90.33 x 10 ³	95.89 x 10 ³
Fe ³⁺	21.54 x 10 ³	14.47 x 10 ³	3.91 x 10 ³	12.03 x 10 ³	20.49 x 10 ³
Fe ²⁺	8.93 x 10 ³	13.52 x 10 ³	8.23 x 10 ³	12.12 x 10 ³	15.85 x 10 ³
Mn	.30 x 10 ³	.38 x 10 ³	.30 x 10 ³	.46 x 10 ³	.61 x 10 ³
Mg	13.75 x 10 ³	11.52 x 10 ³	9.53 x 10 ³	12.54 x 10 ³	16.76 x 10 ³
Ca	30.08 x 10 ³	33.66 x 10 ³	32.37 x 10 ³	33.87 x 10 ³	33.87 x 10 ³
Na	23.66 x 10 ³	23.96 x 10 ³	22.47 x 10 ³	22.55 x 10 ³	22.92 x 10 ³
K	28.80 x 10 ³	19.84 x 10 ³	19.75 x 10 ³	20.83 x 10 ³	21.66 x 10 ³
P	.61 x 10 ³	.65 x 10 ³	.52 x 10 ³	.52 x 10 ³	.52 x 10 ³
Rock position	+8.4	+7.9	+8.6	+7.8	+6.8

respectively. In the latter the values of the function $(\frac{1}{3} \text{Si} + \text{K}) - (\text{Ca} + \text{Mg}) \times 10^{-1}$ for each host rock are given in order to present the «position of the rock» by a modification of the Larsen's method (NOCKOLDS and ALLEN, 1953). The values range between +6.8 and +8.6. It is interesting to observe that these values proved to be in positive correlation with the respective values for the biotites and the hornblendes, as it may be calculated from the Tables 3 and 6. The total number of ions in octahedral sites ($\text{Al}_{\text{iv}} + \text{Ti} + \text{Fe}^{3+} + \text{Fe}^{2+} + \text{Mg} + \text{Mn}$) tends to be in negative correlation with the increasing values of the «rock position».

In Fig. 19 in which data of the chemical analyses of the biotites and the hornblendes have been plotted on the basis $\text{MgO} + \text{Al}_2\text{O}_3 + \text{FeO}_T = 100$, the general trend shows that the ratio $\frac{\text{FeO}_T}{\text{FeO}_T + \text{MgO} + \text{Al}_2\text{O}_3}$ in biotites definitely increases in the passing from the more basic to the

T A B L E 9

Trace / Major-elements ratios for biotites

	L71Bi	L52Bi	F20.Bi	F25Bi	F55Bi
$\text{Ga} \times 10^3 / \text{Al}$.23	.35	.29	.23	.34
$\text{Li} \times 10^3 / \text{Mg}$.65	.32	.26	.32	.25
$\text{Ni} \times 10^3 / \text{Mg}$.30	.36	.37	.28	.45
$\text{Co} \times 10^3 / \text{Mg}$.39	.60	.78	.77	.75
$\text{Fe}^{2+} / \text{Mg}$.92	.76	.81	.83	.84
$\text{Ni} \times 10^3 / \text{Fe}^{2+}$.33	.47	.46	.34	.53
$\text{Co} \times 10^3 / \text{Fe}^{2+}$.42	.78	.97	.92	.89
$\text{Sc} \times 10^3 / \text{Fe}^{2+}$	-	-	-	-	-
$\text{Fe}^{3+} / \text{Fe}^{2+}$.40	.39	.46	.38	.29
$\text{Cr} \times 10^3 / \text{Fe}^{3+}$.79	.56	.88	.87	1.28
$\text{V} \times 10^3 / \text{Fe}^{3+}$	7.94	9.00	8.88	10.32	16.00
$\text{Sr} \times 10^3 / \text{Ca}$	2.66	1.66	-	4.00	-
$\text{Sr} \times 10^3 / \text{Ca} + \text{K}$.16	.14	-	1.36	-
$\text{Ba} \times 10^3 / \text{K}$	50.72	54.68	49.29	49.29	49.29
$\text{Ba} \times 10^3 / \text{Ca} + \text{K}$	47.94	50.00	47.94	47.94	47.94
$\text{Rb} \times 10^3 / \text{K}$	14.49	2.81	1.97	2.53	2.53

more acid rocks. On the other hand the ratio $\frac{\text{Al}_2\text{O}_3}{\text{FeO}_T + \text{MgO} + \text{Al}_2\text{O}_3}$ fairly increases in hornblendes in the same direction. Also, the ratio $\text{Fe}^{3+} / \text{Fe}^{2+}$ (from the Tables 9 and 10) rises in passing from the more basic to the more acid rocks. This was confirmed by an interpretation of some chemi-

cal analyses of these minerals from rhyolites of the island Cos, Dodecanese, Greece (biotite analyses by PECKETT, 1969) and also, from granites and quartz-diorites of Ben-Nevis region, Scotland (biotite and hornblende analyses by HASLAM, 1968). Thus the increase of the ratio proved to be in harmony with the theory that the ratio $\text{Fe}_2\text{O}_3/\text{FeO}$ in the magmatic rocks, rises during the course of the magmatic differentiation (GOLDSCHMIDT edit. by MUIR, 1970). At last the Fe_T tends to become

T A B L E 10
Trace / Major-elements ratios for hornblendes

	L71Ho	L52Ho	F20Ho	F25Ho	F55Ho
$\text{Ga} \times 10^3/\text{Al}$.26	.28	.32	.32	.32
$\text{Li} \times 10^3/\text{Mg}$.35	.35	.64	.27	.27
$\text{Ni} \times 10^3/\text{Mg}$.67	.18	.23	.30	.23
$\text{Co} \times 10^3/\text{Mg}$.40	.30	.38	.48	-
Fe^{2+}/Mg	.74	.73	.72	.78	.83
$\text{Ni} \times 10^3/\text{Fe}^{2+}$.90	.25	.32	.38	.28
$\text{Co} \times 10^3/\text{Fe}^{2+}$.54	.41	.53	.62	-
$\text{Sc} \times 10^3/\text{Fe}^{2+}$	3.03	1.86	3.28	2.77	1.62
$\text{Fe}^{3+}/\text{Fe}^{2+}$.46	.43	.46	.34	.25
$\text{Cr} \times 10^3/\text{Fe}^{3+}$	3.22	.75	1.45	.18	1.35
$\text{V} \times 10^3/\text{Fe}^{3+}$	8.70	7.58	7.09	10.80	16.00
$\text{Sr} \times 10^3/\text{Ca}$	1.23	.81	.82	.18	.30
$\text{Sr} \times 10^3/\text{Ca}+\text{K}$	1.17	.78	.79	.18	.29
$\text{Ba} \times 10^3/\text{K}$	22.72	13.23	226.66	89.65	6.42
$\text{Ba} \times 10^3/\text{Ca}+\text{K}$	1.17	.54	8.29	3.20	.22
$\text{Rb} \times 10^3/\text{K}$	-	-	-	-	-

higher while the Mg tends to become lower in passing from the more basic to the more acid volcanic rocks of W. Thrace both in the biotites and the hornblendes (except F20Ho).

The variations mentioned above were confirmed by an interpretation of the chemical analyses of biotites and hornblendes from the volcanic rocks of Dodecanese (PECKETT, 1969). The reverse phenomenon takes place in the granites and the quartz-diorites from Ben-Nevis (HASLAM, 1968). HASLAM suggests that a constant high partial pressure of oxygen is likely to be the significant factor to the enrichment in Mg of the ferromagnesian minerals during the differentiation course in Ben-Nevis. Also, it is mentioned by MUAN and OSBORN (1956) that the magnesioferrite phase is enriched in Fe during the equilibrium cooling

in a closed system of $\text{MgO} - \text{FeO} - \text{Fe}_2\text{O}_3 - \text{SiO}_2$, but in reverse the same phase is enriched in Mg when oxygen pressure is constant. WONES and EUGSTER (1965) found, by the use of experimental results, that the ratio Fe/Mg slightly falls during crystallization in the system biotite - sanidine - magnetite - melt, if the partial pressure of oxygen is preserved constant. Thus the constant partial pressure of oxygen seems to be the critical factor to the enrichment in Mg of the cases mentioned above. On the other hand, the reverse trends are observed in the Fe and the Mg of the coexisting ferromagnesian minerals of the volcanic rocks of W. Thrace (near the north coast-line of Aegean sea) and Dodecanese (south Aegean sea). Unfortunately data for the conditions of the crystallization course are not available for the volcanic host-rocks of the W. Thrace; while, a definite fall of the oxygen partial pressure with temperature and differentiation have been determined in volcanic rocks from Dodecanese by the use of coexisting magnetite and ilmenite (PECKETT, 1969). Thus departure from a constant partial pressure of oxygen may be again a critical factor to the rise of the Fe and the fall of the Mg in the coexisting hornblendes and biotites in the passing from the more basic to the more acid volcanic host rocks of the Aegean sea. HASLAM (1968) suggests that the presence of hornblende coexisting with biotite and magnetite is also critical in causing the unusual reverse trend in Ben Nevis plutonites. This view could be neglected for the case of the volcanic rocks of W. Thrace wherein magnetite is also observed.

VII. TRACE ELEMENTS (Tables 3 and 6)

For biotites and hornblendes the following schemes of substitution are possible: $\text{Al}^{3+} \leftarrow \text{Ga}^{3+}$, $\text{Fe}^{3+} \leftarrow \text{V}^{3+} \text{Cr}^{3+}$, $\text{Mg}^{2+} \text{Fe}^{2+} \leftarrow \text{Zr}^{4+} \text{Ni}^{2+} \text{Sc}^{3+}$, $\text{Li}^{+} \text{Co}^{2+}$, $\text{Fe}^{2+} \leftarrow \text{Cu}^{2+} (?)$, $\text{Ca}^{2+} \leftarrow \text{Y}^{3+} \text{Sr}^{2+}$, $\text{K}^{2+} \leftarrow \text{Sr}^{2+} \text{Rb}^{+} \text{Ba}^{2+}$.

Thus the bulk of Ga, V, Cr, Zr, Ni, Sc, Li, and Co is believed to substitute for major elements in six-fold coordinated sites although some Ga may substitute for Al in four-fold coordination (DODGE - SMITH - MAYS, 1969). Y, Sr, Rb, and Ba must probably substitute for eight- and twelve-fold coordinated ions in hornblendes and biotites respectively.

Trace elements determinations in the specimens analyzed showed the following results. Sc, Zr, and Y were found in the hornblendes only, while Rb in biotites only. Cr and Cu are lower in the biotites than its associated hornblendes, while Sr, Co, V, Ga, and Ba are higher. Ni and Li are about equally distributed between the coexisting ferromagnesian minerals. The ratios of certain trace elements and associated major elements can be contrasted between the biotites and hornblendes, (see Tables 9 and 10, as in NOCKOLDS and ALLEN, 1958). Thus the ratios

Co/Mg, Ni/Fe²⁺, Sr/Ca + K, Ba/K, Ba/Ca + K, Rb/K, and Sr/Ca are higher in the biotites than its associated hornblendes while the ratio Sc/Fe²⁺ is lower. The ratios Ga/Al, Li/Mg, Ni/Mg, Cr/Fe³⁺, and V/Fe³⁺ tend to be the same in the coexisting ferromagnesian minerals.

Some interesting aspects on the determined trace elements are mentioned in the following lines. In Fig. 20 there is shown the distribution of V between the coexisting biotites and hornblendes from the volcanic rocks of W. Thrace and the gneisses of S. W. QUEBEC (KRETZ,

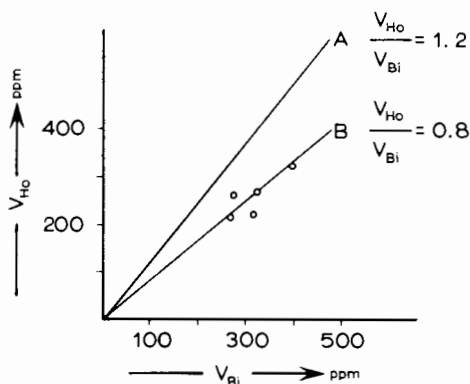


Fig. 20. The distribution of V between coexisting biotites and hornblendes (B = from volcanic rocks of W. Thrace, A = from gneisses of N. W. Quebec).

1959). The Ni ion having the same radius and the same charge as Mg is believed by MASON (1966) to be camouflaged by the latter ion. Y, probably replacing Ca in six-fold and eight-fold coordination (VLASOV, 1966) is found only in hornblendes in which the latter ion is found in the coordination mentioned above. According to the heterovalent isomorphous replacement $\text{Ca}^{2+} + \text{Mg}^{2+} + (\text{Si})^{4+} \leftarrow \text{Na}^{+} + \text{Zr}^{4+} + (\text{Al}, \text{Fe}^{3+})$ proposed by KAKHARENKO et al. (VLASOV, 1966), Zr rises with the increasing values of the ratio $(\text{Al} + \text{Fe})^{3+} / \text{Si}^{4+}$ in the hornblendes analyzed. On the other hand it is mentioned by MASON (1966) that the combination of high charge and comparatively high radius (0.79 Å) set Zr apart from any of the major elements of the igneous rocks. Thus by DODGE, PAPIKE, and MAYS (1968) it has been observed that the small quantities of Zr may merely represent small amounts of zircon included in the hornblendes. Also, the ratio $\text{Al}^{3+} / \text{Si}^{4+}$ tends to rise with the increasing values of Sc in the analyzed hornblendes in harmony with the heterovalent isomorphous replacement (VLASOV, 1966) $(\text{Fe}, \text{Mg})^{2+} + \text{Si}^{4+} \leftarrow \text{Sc}^{3+} + \text{Al}^{3+}$. Rb which can replace K only is found in the

biotites only. Also Ba can substitute for K only (MASON, 1966). However, Ba is determined both in the biotites and the hornblendes, but in great concentration in the former (3,500 ppm) and small in the latter mineral (an average of 220 ppm). At last the ionic radius of the Cu (0.72\AA) is comparable with that of the bivalent iron but its electronegativity is very high (1.8 or 2.0). Thus such elements as Mg^{2+} , Fe^{3+} or Mn^{3+} with lower electronegativity (1.2, 1.6, and 1.4 respectively) are preferentially incorporated because they form stronger and more ionic bonds than Cu.

There are observed the following relations between the trace elements of the coexisting ferromagnesian minerals and their host volcanic rocks from W. Thrace.

Biotites: The following ratios, only tend to increase in the passing from the more basic to the more acid rocks, Li/Mg and Rb/K ; while the following tend to decrease Ga/Al , Co/Mg , Ni/Fe^{2+} , Cr/Fe^{3+} , Co/Fe^{2+} . The ratios Ni/Mg , Ba/K , $\text{Ba/Ca} + \text{K}$, Sr/Ca , and $\text{Sr/Ca} + \text{K}$ remain fairly constant.

Hornblendes: The following ratios tend to increase in the passing from the more basic to the more acid rocks, Li/Mg , Sc/Fe^{2+} , $\text{Sr/Ca} + \text{K}$, $\text{Ba/Ca} + \text{K}$, and Y/Ca ; while the following ratios tend to decrease in the same direction Cr/Fe^{3+} , V/Fe^{3+} and Co/Mg . The ratios Ga/Al , Ni/Mg , Ni/Fe^{2+} and Co/Fe^{2+} remain fairly constant.

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ΠΕΡΙΛΗΨΙΣ

Ἡ παρῶσα μελέτη ἀναφέρεται εἰς τὴν χημικὴν σύστασιν καὶ τὴν γεωχημείαν κεροσιλιβῶν καὶ βιοτιτῶν συνυπαρχόντων ὡς τῶν μοναδικῶν σιδηρομαγνησιούχων ὄρυκτῶν ἐντὸς δειγμάτων ἡφαιστειακῶν πετρωμάτων ἐκ τῆς Δυτικῆς Θράκης. Δίδονται αἱ χημικαὶ ἀναλύσεις, οἱ χημικοὶ τύποι καὶ ἡ συμμετοχὴ τῶν διαφόρων στοιχείων εἰς ppm, τῶν ἀναλυθέντων δειγμάτων. Ἡ μεταβολὴ τῆς

περιεκτικότητας εις τὰ διάφορα στοιχεία διερευνᾶται συναρτήσει τοῦ συνόλου τῶν ιόντων τῆς Υ ὁμάδος.

Οἱ βιοτίται παρουσιάζουν ἀσθενῆ ἀλλὰ σαφῇ ὑπεροχὴν τοῦ Mg ἔναντι τῶν ὑποκαταστατῶν του εἰς τὰς ὀκταεδρικὰς θέσεις ἐνῶ τὸ Si ὑποκαθίσταται ὑπὸ τοῦ Al εἰς ἀναλογίαν 5,5 : 2,5 εἰς τὰς τετραεδρικὰς θέσεις. Ἡ ὑποκατάστασις τοῦ Si ὑπὸ τοῦ Al εἰς τὰς τετραεδρικὰς θέσεις δημιουργεῖ ἔλλειμμα θετικῶν φορτίων τὸ ὁποῖον καλύπτεται διὰ τῆς παρατηρουμένης αὐξήσεως τοῦ συνόλου τῶν ιόντων τῆς Υ ὁμάδος, μὴ ὑπαρχούσης αὐξήσεως τῆς συμμετοχῆς τρισθενῶν ἢ τετρασθενῶν ιόντων τῆς ὁμάδος ταύτης. Εἰς τὰ δείγματα L52 καὶ L71 τὸ σύνολον τῶν θετικῶν φορτίων τῆς ὁμάδος Υ εἶναι μικρότερον τῶν ἄλλων δειγμάτων καὶ οὕτως παρατηρεῖται μία αὐξησης τῆς ἀναλογίας O : OH, F καὶ τῆς συμμετοχῆς τοῦ Ca εἰς τὴν X ὁμάδα. Ἀποδεικνύεται ἡ συστηματικὴ συμμετοχὴ τοῦ Ca εἰς τὸ κρυσταλλικὸν πλέγμα τῶν βιοτιτῶν τῶν ἐξετασθέντων δειγμάτων διὰ τῆς σαφοῦς ἀντιπαθητικῆς σχέσεως ἡ ὁποία ὑπάρχει μεταξὺ Ca καὶ K ὡς καὶ Ca + Sr καὶ K. Ἡ σχέσις Mg : Fe καὶ τὸ σύνολον τῶν ἀλκαλικῶν γαιῶν αὐξάνει πρὸς τοὺς περισσότερον Mg- βιοτίτας.

Αἱ κεροσιλβίαι παρουσιάζουν μεγάλην συμμετοχὴν Ca καὶ κατατάσσονται εἰς τὰς Ca-πλουσίας τοιαύτας. Μία στενὴ σχέσις παρατηρεῖται εἰς τὰς ὑποκαταστάσεις τοῦ τρισθενοῦς Fe, τοῦ Mg, τοῦ δισθενοῦς Fe καὶ τοῦ Al εἰς ὀκταεδρικὰς θέσεις. Μία ἀντιπαθητικὴ σχέσις ὑπάρχει μεταξὺ Ca καὶ Mg. Ἡ ὑποκατάστασις τοῦ Si ὑπὸ τοῦ Al εἰς τετραεδρικὰς θέσεις δημιουργεῖ καὶ εἰς τὴν περίπτωσιν τῶν κεροσιλβίων ἔλλειψιν θετικῶν φορτίων. Τὸ ἔλλειμμα τοῦτο καλύπτεται διὰ τῆς αὐξήσεως τῆς συμμετοχῆς τῶν τρισθενῶν καὶ τετρασθενῶν ιόντων τῆς Υ ὁμάδος καὶ τῶν ἀλκαλίων εἰς τὰς Α θέσεις. Ὅπωςδήποτε ἡ συμμετοχὴ περισσοτέρων τῶν 2,000 ιόντων εἰς τὰς Α θέσεις δὲν ἐξαρτᾶται ἀπὸ τὰς μεταβολὰς τῆς συμμετοχῆς ἐτέρων ιόντων καὶ εἰκάζεται ὅτι τὸ ἔλλειμμα τῶν φορτίων καλύπτεται κατὰ προτίμησιν ὑπὸ στοιχείων τῆς ὁμάδος Υ.

Εἰς τοὺς βιοτίτας παρατηρεῖται μία μεγαλυτέρα ἀνοχὴ εἰς τὴν μεταβολὴν τοῦ ἀριθμοῦ τῶν ιόντων τῆς Υ ὁμάδος ἐν συγκρίσει μετὰ τῶν συνυπαρχουσῶν κεροσιλβίων καὶ οὕτως ἐρμηνεύεται ὁ διάφορος τρόπος καλύψεως τῶν ἐλλείψεων φορτίων μεταξὺ τῶν ὀρυκτῶν τούτων. Ἡ γραμμικὴ σχέσις ἡ ὁποία ὑφίσταται μεταξὺ τῶν συνόλων τῶν ιόντων τῶν Υ ὁμάδων τῶν κεροσιλβίων καὶ βιοτιτῶν δεικνύει ὅτι ἡ αὐξησης τῆς συμμετοχῆς τῶν ιόντων εἰς τὴν Υ ὁμάδα ἐξαρτᾶται ἐκ τῆς ἰδίας αἰτίας τῶν εἰδικῶν συνθηκῶν τῶν δημιουργουμένων κατὰ τὴν πορείαν τῆς κρυσταλλώσεως τῶν διαφόρων μαγματικῶν τηγμάτων.

Παρατηρεῖται τάσις αὐξήσεως τοῦ ὀλικοῦ ἀριθμοῦ τῶν ιόντων εἰς τὴν Υ ὁμάδα τῶν σιδηρομαγνησιούχων ὀρυκτῶν συναρτήσει τῆς βασικότητος τῶν πετρωμάτων.

Ἡ μεταβολὴ τῆς ἀναλογίας συμμετοχῆς τοῦ τρισθενοῦς Fe ἔναντι τοῦ δισθενοῦς εἰς τὰ συνυπάρχοντα ὀρυκτὰ ἐκ τῶν βασικωτέρων πρὸς τὰ ὀξινότερα πετρώματα, εὐρίσκεται εἰς ἁρμονίαν μετὰ τῆς θεωρίας τῆς αὐξήσεως τῆς συμμετοχῆς τοῦ Fe_2O_3 ἔναντι τοῦ FeO κατὰ τὴν διάρκειαν τῆς μαγματικῆς διαφορο-

ποιήσεως. Ἐξ ἄλλου παρατηρεῖται τάσις μειώσεως τῆς συμμετοχῆς τοῦ Mg ἔναντι τῆς ἀντιστοίχου τοῦ Fe εἰς τὰ ἐξετασθέντα ὄρυκτά κατὰ τὴν πορείαν ἐκ τῶν βασικωτέρων πρὸς τὰ ὀξινότερα πετρώματα καὶ ἡ ὁποία ἀποδίδεται εἰς τὴν μείωσιν τῆς μερικῆς πιέσεως τοῦ ὀξυγόνου συναρτῆσει τῆς ἐξελίξεως τῆς διαφοροποιήσεως καὶ τῆς πτώσεως τῆς θερμοκρασίας.

Ἰχνοστοιχεῖα ἐντὸς τῶν βιοτιτῶν καὶ τῶν κεροστιλβῶν.

Σκάνδιον, Ζιρκόνιον καὶ Ὑττριον προσδιωρίσθησαν μόνον εἰς τὰς κεροστίλβας ἐνῶ Ρουβίδιον εἰς τοὺς βιοτίτας. Τὸ Χρῶμιον καὶ ὁ Χαλκὸς εὐρίσκονται εἰς μικροτέραν ἀναλογίαν ἐντὸς τῶν βιοτιτῶν ἐνῶ τὰ στοιχεῖα Στρόντιον, Κοβάλτιον, Βανάδιον, Γάλλιον καὶ Βάριον εἰς μεγαλυτέραν ἐν συγκρίσει πρὸς τὰς συνυπαρχούσας κεροστίλβας. Τὸ Νικέλιον καὶ τὸ Λίθιον ἀνευρίσκονται εἰς τὰς ἰδίας περίπου ἀναλογίας. Παρατηρήθησαν ἐνδιαφέρονσαι σχέσεις εἰς τὰς συμμετοχὰς τῶν στοιχείων εἰς ἔχνη. Τὸ Ὑττριον τὸ ὁποῖον ὑποκαθιστᾷ τὸ Ἀσβέστιον εἰς τετραεδρικός ἢ ὀκταεδρικός θέσεις προσδιωρίσθη μόνον εἰς τὰς κεροστίλβας, εἰς τὰς ὁποίας τὸ δευτερον στοιχεῖον τοποθετεῖται εἰς ἀντιστοίχους θέσεις. Ἀντιθέτως τὸ Ρουβίδιον τὸ ὁποῖον ὑποκαθιστᾷ τὸ Κάλιον ἀνευρέθη εἰς τοὺς βιοτίτας. Ἡ συμμετοχὴ τοῦ Ζιρκονίου εἰς τὰς κεροστίλβας αὐξάνει συναρτῆσει τῆς ἀναλογίας $(Al + Fe)^{3+} : Si^{4+}$ εἰς ἀντιστοιχίαν μετὰ τῆς ἑτεροσθενοῦς ἰσομόρφου ὑποκαταστάσεως $Ca^{2+} + Mg^{2+} + (Si)^{4+} \leftarrow Na^{+} + Zr^{4+} + (Al, Fe)^{3+}$. Ἡ συμμετοχὴ τοῦ Σκανδίου αὐξάνει ἀναλόγως τῆς σχέσεως $Al^{3+} : Si^{4+}$ ἐν ἁρμονίᾳ μετὰ τῆς ἑτεροσθενοῦς ἰσομόρφου ὑποκαταστάσεως $(Fe, Mg)^{2+} + Si^{4+} \leftarrow Sc^{3+} + Al^{3+}$.

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