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RELATION OF ATOMIC CONSTITUTION TO LATTICE PARAMETERS IN
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INTRODUCTION

The biggest obstacle to elaborate geochemical studies on minerals is the enormity of time and expense involved in obtaining a large number of analyses by the wet chemical method. To overcome this, attempts have been made to determine chemical composition indirectly by finding and measuring easily determinable physical properties that may be related to composition.

Over the last decade several workers attempted to employ certain structural parameters, quickly determinable by *x*-ray diffractometric methods, for the determination of mineral compositions. Claisse (1950), Goodyear and Duffin (1954, 1955), Smith (1956), Smith and Yoder (1956) and others have discussed the determination of composition of plagioclases by means of *x*-ray powder diffraction patterns. Gower (1957) claimed that the iron-magnesium ratio in biotites may be determined to about 5% or better accuracy by measuring the ratio of the intensities of the (004)/(005) reflections. Hess (1952) in his studies on orthopyroxenes found a general correlation of unit cell dimensions with ion substitution and composition. There is no report in the literature regarding similar studies on hornblendes; so an attempt was made to find any possible correlation between unit cell dimensions and chemical composition in hornblendes.

The work was carried out in the Division of Geological Sciences, California Institute of Technology, during the summer of 1958. Helpful discussions with Drs. A. E. J. Engel and Barclay Kamb are gratefully acknowledged.

HORNBLENDES STUDIED

Altogether six hornblendes were separated from samples of amphibolite occurring as irregular masses enclosed in pelitic schists in which three zones of progressive metamorphism can be recognized. These schists and amphibolites constitute a small Precambrian inlier peeping out through younger sediments near Lead, Black Hills, South Dakota (Noble and Harder, 1948).

Samples H1 and H5 come from the lowest part of the garnet zone, whereas sample H61 comes from upper-middle part of the garnet zone.

TABLE 1. CHEMICAL ANALYSES OF 6 HORNBLENDES

	H-1	H-5	H-61	H-70	H-72	H-78
SiO ₂	45.20	45.20	45.00	46.01	44.17	42.71
Al ₂ O ₃	13.49	13.00	14.66	11.88	13.29	15.15
TiO ₂	0.43	0.44	0.48	0.43	0.78	0.66
Fe ₂ O ₃	1.93	2.04	1.15	1.89	1.99	2.90
FeO	12.10	12.89	11.83	13.96	14.91	17.53
MnO	0.23	0.19	0.23	0.23	0.25	0.56
MgO	11.45	11.39	11.68	10.26	9.07	6.22
CaO	11.39	10.99	11.64	12.03	11.49	10.59
Na ₂ O	1.20	1.12	1.12	0.72	1.10	1.62
K ₂ O	0.25	0.25	0.22	0.59	0.37	0.26
H ₂ O ⁺	2.04	2.01	1.90	1.73	2.16	1.40
H ₂ O ⁻	0.00	0.04	0.00	0.02	0.02	0.00
F	0.04	0.03	0.04	0.20	0.04	0.20
Cl	0.01	tr	n.d.	n.d.	n.d.	tr
O	99.76	99.59	99.95	99.95	99.64	99.80
(F and Cl)	0.02	0.01	0.02	0.08	0.02	0.08
Total	99.74	99.58	99.93	99.87	99.62	99.72

Analyst: C. O. Ingamells, Rock Analysis Laboratory, University of Minnesota.

tr = trace.

n.d. = not determined.

Samples H78 and H70 are from the uppermost part of the garnet zone, and sample H72 was collected from well within the staurolite zone.

All the six hornblendes were analyzed chemically by wet chemical methods (Table 1). Structural formulae of the six hornblendes were also calculated in the standard way on the basis of 24 O, OH, F and Cl ions in the formula (Table 2). As is evident, all the six hornblendes should be classified as femag-hastingsite.

EXPERIMENTAL METHODS

Unit cell parameters $a \sin \beta$, b and $c \sin \beta$ for the hornblendes were determined from powder patterns. $a \sin \beta$ was determined from reflection (600), b from (0,10,0) and $c \sin \beta$ from (002). The powder work was done with a Norelco geiger counter x-ray diffractometer using nickel filtered Cu-radiation at 40 kv and 15 ma, scanning speed $\frac{1}{8}$ degree per minute, chart speed $\frac{1}{2}$ inch per minute, time constant 8 seconds, divergent slit 4 degrees, receiving slit .006 inch and scatter slit 1 degree.

Each of the three reflections of each sample, was scanned four times, each time with a different powder pack of the same sample, and the val-

TABLE 2. STRUCTURAL FORMULAE OF ANALYZED HORNBLENDES
 (Structure Type $X_{0-1}A_2B_3C_8Y_{24}$)

		H-1	H-5	H-61	H-70	H-72	H-78
X	Na ¹⁺	.250	.243	.314	.200	.167	.447
	K ¹⁺	.052	.053	.035	.106	.071	.054
	Ca ²⁺	—	—	.009	—	—	—
	0-1	.302	.296	.358	.306	.238	.501
A	Ca ²⁺	1.777	1.720	1.803	1.901	1.822	1.717
	Fe ²⁺	.114	.181	.171	.061	—	.185
	Na ¹⁺	.083	.073	—	.012	.153	.025
	Mn ²⁺	.026	.026	.026	.026	.025	.073
	2	2	2	2	2	2	2
B	Mg ²⁺	2.487	2.475	2.526	2.246	1.999	1.399
	Fe ²⁺	1.357	1.390	1.266	1.655	1.848	2.032
	Al ³⁺	.902	.854	1.034	.843	.841	1.169
	Fe ³⁺	.210	.228	.122	.212	.213	.327
	Ti ⁴⁺	.044	.053	.052	.044	.089	.073
	Mn ²⁺	—	—	—	—	.010	—
	5	5	5	5	5	5	5
C	Si ⁴⁺	6.591	6.608	6.525	6.774	6.531	6.461
	Al ³⁺	1.409	1.392	1.475	1.226	1.469	1.539
	8	8	8	8	8	8	8
Y	O ²⁻	22.001	22.020	22.154	22.205	21.849	22.574
	OH ¹⁻	1.978	1.966	1.829	1.698	2.133	1.417
	F ¹⁻	.018	.014	.017	.097	.018	.009
	Cl ¹⁻	.003	trace	—	—	—	trace
	24	24	24	24	24	24	24

ues were averaged. In preparing each powder pack extreme care was taken to make the powder surface as flat as possible and in plane with the surface of the holder, thus making the geometrical condition between packs as reproducible as possible. It was found that peak locations from different packs of the same sample could be reproduced within 0.02 degree 2θ in most cases. Since the samples had to be saved for other work, no internal standards were used, to avoid contamination. But spectroscopically pure NaCl was run under identical experimental conditions and the

observed d -values of the reflections from it were compared with the corresponding values of NaCl given by Swanson and Fuyat (1953, p. 43) to calculate the instrumental error. Averaging results from three different runs of NaCl, the total instrumental correction in d in the 2θ regions of (600), (0,10,0) and (002) reflections from hornblendes were calculated as -0.0020 \AA , -0.0029 \AA and -0.004 \AA respectively. The corresponding corrections for the $a \sin \beta$, b and $c \sin \beta$ values were thus -0.012 \AA , -0.029 \AA and -0.008 \AA respectively. The corrected cell dimensions and their averages are given in Table 3. Assuming a maximum error of ± 0.02 degree in 2θ values, the possible errors in $a \sin \beta$, b and $c \sin \beta$ were calculated as $\pm 0.003 \text{ \AA}$, $\pm 0.007 \text{ \AA}$ and $\pm 0.003 \text{ \AA}$ respectively. Table 3 also shows the number of octahedral Fe^{2+} ions, octahedral ($\text{Al}^{3+} + \text{Fe}^{3+}$) ions and tetrahedral Al^{3+} ions per unit cell of the six hornblendes. As there are

TABLE 3. UNIT CELL DIMENSIONS OF ANALYZED HORNLENDES

Sample No	$a \sin \beta$ Å	mean $a \sin \beta$ Å	b Å	mean b Å	$c \sin \beta$ Å	mean $c \sin \beta$ Å	Octa- hedral Fe^{2+} per unit cell	Octa- hedral (Al^{3+} + Fe^{3+}) per unit cell	Tetra- hedral Al^{3+} per unit cell
H-1	9.500	9.500	18.064	18.063	5.104	5.104	2.714	2.224	2.818
	9.498		18.060		5.102				
	9.501		18.065		5.106				
	9.501		18.064		5.106				
H-5	9.515	9.515	18.041	18.040	5.098	5.101	2.780	2.164	2.784
	9.517		18.043		5.102				
	9.513		18.039		5.101				
	9.515		18.037		5.102				
H-61	9.512	9.511	18.024	18.027	5.096	5.097	2.532	2.312	2.950
	9.511		18.029		5.096				
	9.510		18.029		5.098				
	9.510		18.025		5.098				
H-70	9.508	9.507	18.087	18.086	5.100	5.098	3.310	2.110	2.452
	9.505		18.085		5.096				
	9.509		18.090		5.100				
	9.505		18.083		5.098				
H-72	9.523	9.521	18.087	18.088	5.108	5.107	3.696	2.108	2.938
	9.519		18.085		5.105				
	9.523		18.091		5.108				
	9.521		18.089		5.106				
H-78	9.536	9.536	18.046	18.049	5.111	5.110	4.064	2.992	3.078
	9.534		18.048		5.108				
	9.538		18.052		5.111				
	9.535		18.049		5.109				

Assuming a possible error of ± 0.02 degree in 2θ values possible error in $a \sin \beta$ is $\pm 0.003 \text{ \AA}$, in b is $\pm 0.007 \text{ \AA}$ and in $c \sin \beta$ is $\pm 0.003 \text{ \AA}$.

two formula units per unit cell of hornblende, the number of each of these ions per unit cell was obtained by doubling the number of the same ion in the structural formula.

DISCUSSION

By far the most important substitution of cations in hornblendes (structure type $X_{0-1}A_2B_5C_8Y_{24}$) is the replacement of Mg by Fe in the octahedral site. This substitution may be a simple replacement of Mg^B by $Fe^{(2+)B}$ or a part of the paired substitution $Mg^B Si^C$ by $Fe^{(3+)B} Al^C$. The other important substitution is the replacement of Si by Al in the tetrahedral site which is a part of the paired substitution either $Na^X Al^C$ for Si^C or $Al^B Al^C$ [or $Fe^{(3+)B} Al^C$] for $Mg^B Si^C$. In the hornblendes of this study up to 14% of the lime is replaced by Na^{1+} , Fe^{2+} and Mn^{2+} . Whether this substitution of Ca by Na is part of the paired substitution $Na^X Na^A$ for Ca^A or $Na^A Al^B$ for $Ca^A Mg^B$, cannot be decided. As a consequence the exact extents of the substitutions $Na^X Al^C$ for Si^C and $(Al^{3+}, Fe^{3+})^B Al^C$ for $Mg^B Si^C$ cannot be determined. Ti replaces Mg probably as part of the substitution $Ti^B Al^C Al^C$ for $Mg^B Si^C Si^C$ or $Na^A Na^A Ti^B$ for $Ca^A Ca^A Mg^B$.

An inspection of the structural formulae of the six hornblendes given in Table 2 shows that the most extensive substitutions in these hornblendes are the replacement of Mg^{2+} by Fe^{2+} in the octahedral site, the replacement of Si^{4+} by Al^{3+} in the tetrahedral site and the substitution of (Al^{3+}, Fe^{3+}) for Mg^{2+} in the octahedral site. The extreme absolute differences in the extents of these substitutions within these six hornblendes, are also much greater than similar extreme absolute differences in the extents of other cation substitutions. Besides, the total extents of the other cation substitutions are very small except in case of the replacement of Ca^A by $(Na^{1+}, Fe^{2+}, Mn^{2+})$.

The above observations together with a comparison of the radii¹ of the various substituting ions, make it seem most likely that in these hornblendes the variations in the lattice parameters, in as much as such variation is controlled by ionic substitution, are due mainly to variations in the amount of replacement of the constituent ions by larger or smaller ions. These replacements involve the replacement of smaller Mg^{2+} by larger Fe^{2+} at the octahedral site, the replacement of smaller Si^{4+} by larger Al^{3+} at the tetrahedral site and the replacement of larger Mg^{2+} by smaller Al^{3+} (and Fe^{3+}) at the octahedral site.

It may be generally expected that the substitution of the larger Fe^{2+} for the smaller Mg^{2+} at the octahedral site would increase the dimensions of a and b , whereas the substitution of the smaller Al^{3+} (also Fe^{3+}) for the larger Mg^{2+} at the same site would produce opposite effects. Similarly it

¹ See, for example, Ahrens, *Geochim. Cosmochim. Acta*, 2, 168, 1952.

may be expected that substitution of the larger Al^{3+} for the smaller Si^{4+} at the tetrahedral site would increase the length of the Si_4O_{11} double chains and hence c . Hess (1952, p. 176–177, 186), in his studies of the changes in unit cell dimensions as a function of ion substitutions in orthopyroxenes of the Bushveld type, found that in samples with approximately the same R_2O_3 weight per cent the substitution of Fe^{2+} for Mg^{2+} in the structure results in a regular increase in the size of all three dimensions, a , b and c but is comparatively smaller for c than for the other two. He further found that b decreases regularly with the substitution of the smaller Al^{3+} for larger Mg^{2+} and that in replacing Mg^{2+} at the octahedral site, larger ion (other than Fe^{2+}) only increases a and smaller ion only decreases b . Hess also found that:

“The ‘ c ’ dimension seems to be affected by small amounts of Al^{3+} but after R_2O_3 reaches something less than $2\frac{3}{4}$ per cent by weight, further increase is not observed in ‘ c ’. The substitution of the larger Al^{3+} ion for the smaller Si^{4+} ion at first increases the length of the $-\text{SiO}_3$ chains but larger amounts of Al^{3+} possibly cause the $-\text{SiO}_3$ chains to zigzag in the (010) plane. Zigzag in this plane is further suggested by the lack of change of ‘ a ’, though the Mg^{2+} ions are being replaced by smaller Al^{3+} ions and the conspicuous contraction of ‘ b ’.”

Assuming that β for all the six hornblendes of this study is very much the same, the c dimensions of all six are not appreciably different from each other, considering the limits of error. It is, however, interesting to note that leaving out specimen H61, the mean $c \sin \beta$ values of the other five show a regular but very slight increase with increase of tetrahedral Al^{3+} ions per unit cell. In Fig. 1 octahedral Fe^{2+} ions per unit cell have been plotted against the $a \sin \beta$ value of the corresponding cell. Admittedly, the points do not fall on a smooth curve, but a general suggestion of increase in a with increase in Fe^{2+} is discernible. If the ratio octahedral Fe^{2+} /octahedral ($\text{Al}^{3+} + \text{Fe}^{3+}$), instead of only octahedral Fe^{2+} per unit cell, is plotted against the $a \sin \beta$ value of the corresponding cell, it is found that the points become more scattered and deviate from a smooth curve. This may mean, as Hess found in the case of his orthopyroxenes, that in replacement of Mg^{2+} at the octahedral site smaller ion decreases only b and not a . In Fig. 2 the ratio of octahedral Fe^{2+} to octahedral ($\text{Al}^{3+} + \text{Fe}^{3+}$) ions per unit cell has been plotted against b value of the corresponding cell. The resulting regression line seems to support the contention that, qualitatively at least, b increases with the substitution of Fe^{2+} for Mg^{2+} and decreases with the substitution of (Al^{3+} , Fe^{3+}) for Mg^{2+} at the octahedral site. These conclusions also are similar to those arrived at by Hess in his study of the orthopyroxenes.

The effects of pressure on cell dimensions of hornblendes are not known. Crowley and Roy (1958) believe that the cell dimensions of syn-

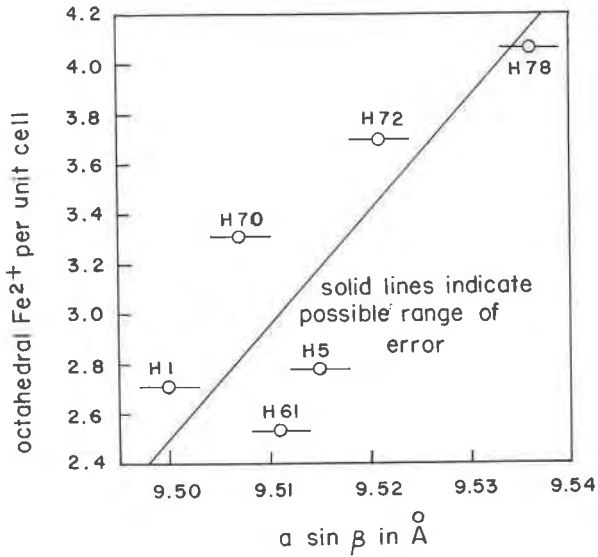


FIG. 1. Relation of $a \sin \beta$ of unit cell to octahedral Fe^{2+} ions per unit cell in hornblendes.

thetic micas are a reproducible function of the pressure of formation. No similar data are available in case of hornblende. If pressure has any appreciable effect in determining cell dimension, the relative importance of this with respect to the effects on cell dimensions due to variations in

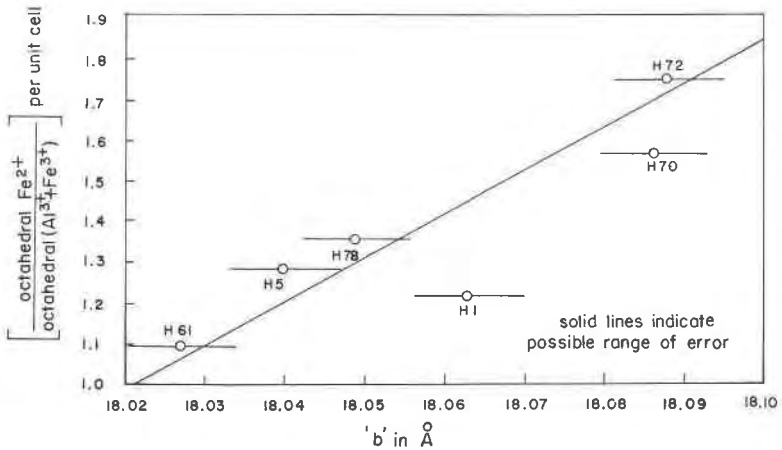


FIG. 2. Relation of b of unit cell to octahedral Fe^{2+} /octahedral $(Al^{3+} + Fe^{3+})$ ions per unit cell in hornblendes.

chemical composition in natural situations encountered with metamorphic rocks, is even more difficult to resolve. Engel and Engel (1960) report decrease in size of unit cell of biotites with increasing grade of metamorphism but opine that the change may also be related to the accompanying increase in fluorine content of the biotites from lower to the higher grade of metamorphism. Yoder and Eugster (1954) and Gower (1957) have clearly established that increase in fluorine content of biotites is accompanied by a marked decrease in dimension of the unit cell.

In Fig. 3, $a \sin \beta$ and b of the hornblendes have been plotted against their metamorphic ranks measured in terms of distances of the sample locations from the garnet isophase. No obvious trends can be established.

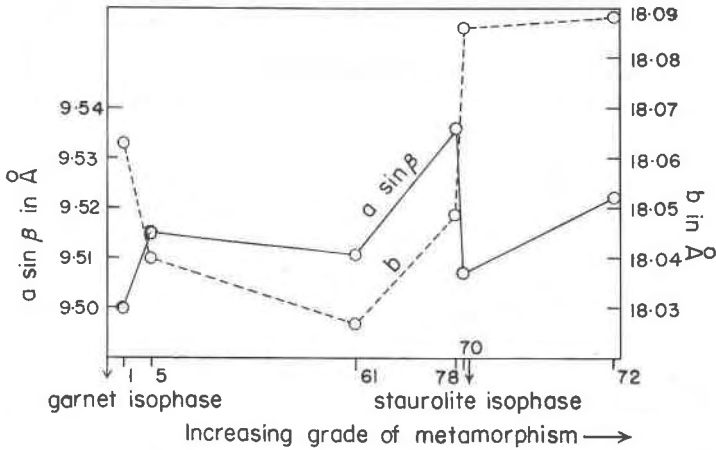


FIG. 3. Unit cell parameters of hornblendes plotted against grade of metamorphism.

A more reliable way of checking the true relationships would have been to arrange the data into a number of groups representing different regions of the metamorphic range encountered and to compare the average values of such groups. But in the present case the quantity of available data is inadequate for such treatment. Ordinarily, higher pressure at the higher grades of metamorphism (if this correlation is always true) should tend to decrease the unit cell volume. Whether or not such reduction of cell volume in hornblendes can be accomplished by increasing pressure without accompanying change of chemical composition is not known and needs to be explored by laboratory experiment. If decrease in cell volume induced by higher pressure is accomplished through reduction of cell dimensions by suitable readjustment of chemical constitution, then in hornblendes higher pressure of formation should facilitate the substitution $\text{Al}^{\text{B}}\text{Al}^{\text{C}}$ for $\text{Mg}^{\text{B}}\text{Si}^{\text{C}}$ and inhibit the substitution $\text{Fe}^{(2+)^{\text{B}}}$ for Mg^{B} . In the case of the

hornblendes of this study the octahedral Al^{3+} contents do not show any such relation with increasing grade of metamorphism and their octahedral Fe^{2+} content is actually higher in the higher grades. But this difference in iron content may very well be due to differences in the original bulk compositions of the amphibolites swamping less conspicuous chemical differences induced by varying conditions of metamorphism.

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LATTICE PARAMETERS AND EXPANSION COEFFICIENTS OF FeS_2
(NATURAL AND SYNTHETIC), AND OF CoS_2

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SOME PREVIOUS INVESTIGATIONS

Lattice parameter determinations of various pyrites were made by many investigators, e.g. Peacock and Smith (1941), Wasserstein (1949),