

Hornblendic amphiboles from basic and intermediate rocks of Swat-Kohistan, northwest Pakistan

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Abstract

Chemical analyses for 21 elements together with physical data are presented for 38 amphiboles (34 of them new) from garnet granulites, pyroxene granulites, amphibolites, and quartz diorites constituting the southern half of the Kohistan Cretaceous–Early Tertiary arc. The metamorphic hornblendes are rich in alumina and some of them have high Al^{VI}/Al^{IV} ratios. The elements in the amphiboles are studied in relation to each other and to those of their host rocks. The Mg/Fe ratio is strongly dependent, and Fe^{3+} and K partly dependent upon bulk chemistry, whereas Ca and Na are relatively independent of the chemistry of the host rock. The amounts of Al, Ti, and Na are controlled to a large extent by bulk mineralogy and to a lesser extent by bulk composition. The influence of metamorphic conditions is not important except on A-site occupancy and, possibly, on Ti and Mn contents. Other factors having variable influence on these components are also discussed. Refractive indices, birefringence, and density display a systematic increase (and 2V a decrease) with decrease in the ratio $(Mg + Al^{VI})/(Mg + Al^{IV} + Al^{VI} + Ti + Fe^{3+} + Fe^{2+} + Mn)$. Pleochroic colors and amount of absorption are controlled by Fe^{3+} , Ti, Fe^{3+}/Ti , and Mg/Fe^{2+} , while Z:c appears to increase with $Fe^{3+} + Ca$.

Introduction: general geology

The northern parts of Swat and Kohistan districts, northern Pakistan, are principally occupied by variously metamorphosed basic to intermediate rocks. Along a 70 km course of the Swat river there are three NE-trending belts consisting, from south to north, of amphibolites, pyroxene granulites, and quartz diorites. These rocks extend E–W for more than 250 km between Nanga Parbat and eastern Afghanistan (see maps in Jan and Kempe, 1973; Takhirheli and Jan 1979; Coward *et al.*, 1982). In the south the amphibolites are thrust faulted upon Precambrian to Palaeozoic sialic metasediments and younger granitic rocks. The occurrence of blueschists, serpentinites and other ultramafic rocks along this thrust fault is suggestive of major tectonic activity (*cf.* Coleman, 1971, 1972; Moores, 1973) and the fault is now considered to be an extension of the Indus suture which marks the

subduction of the Indian plate under the “Asiatic” mass (Jan, 1977, 1980; Takhirheli *et al.*, 1979).

Along the Indus River near Jijal (35°05'N, 72°22'E), the amphibolites are separated from the Indian plate by a fault-bounded 200 sq. km wedge of garnet granulites and alpine ultramafic rocks, which constitute the Jijal complex. To the north of the basic and intermediate rocks of Swat–Kohistan are found variously metamorphosed basic, intermediate, and acidic plutonic and volcanic rocks and sediments, marked again by a major thrust with associated ophiolite melange. To the north of this thrust, sedimentary and Cretaceous–Tertiary granitic rocks occur, which may represent an Asiatic mass, a Gondwanic micro-continent or Tethyan metasediments. A recent interpretation of the metaigneous rocks with subordinate metasediments between the two thrusts suggests that they represent a Late Cretaceous–Early Tertiary island arc sandwiched between the Indian and Asian plates (Ta-

hirkheli *et al.*, 1979; Bard *et al.*, 1980; Jan, 1980 but see also Coward *et al.*, 1982).

The garnet granulites are mostly basic rocks consisting of garnet + plagioclase + clinopyroxene and/or amphibole + quartz + rutile ± epidote but some are composed of only two or more of the mafic silicate minerals. They are considered to have equilibrated at 670° to 790°C and 12 to 14 kbar (Jan and Howie, 1981). The pyroxene granulites consist of plagioclase (~An₅₀), ortho- and clinopyroxene with generally subordinate amounts of amphibole, biotite, quartz, and K-feldspar and have equilibrated at about 800°C and 7 to 8 kbar (Jan and Howie, 1980). The quartz diorites are essentially composed of intermediate plagioclase, quartz, hornblende and/or biotite, with pyroxene in some. Temperature estimates for these rocks, based solely on the plagioclase-amphibole geothermometer of Perchuk (1966) and Spear (1980), raise the possibility that most of them may have finally equilibrated at submagmatic temperatures (540° to 650°C). The amphibolites consist of amphibole, plagioclase and/or epidote, with variable amounts of garnet, micas, *etc.* They are homogeneous to banded and range from "hornblendites" to amphibole-bearing quartzofeldspathic gneisses metamorphosed generally between 570° and 670°C and 4 to 6 kbar (Jan, 1977).

This paper presents an account of 38 calcic amphiboles from the four rock-types, more than half being from amphibolites. The optical properties and density of the amphiboles have been related to their chemistry. Cation correlation within the amphiboles as well as with those of their host rocks are discussed in detail along with other chemical features. Further details of petrography, petrology and mineralogy of rocks of Swat-Kohistan can be found in the relevant literature cited above.

Analytical techniques

Disc and Frantz magnetic separators and heavy liquids were used for mineral separation. Only those rocks were chosen for separation which showed an equilibrium texture and in which the minerals, especially plagioclase, showed no (or only marginal) zoning. The minerals were finely ground to between 200 and 300 B.S.M. in order to break off adjoining grains and inclusions. In most cases the analyzed concentrates were purer than 99% (as estimated by grain counts). Comments on the impurities are given in Appendix 1.

Density was determined by using about 3.0 g of material in a pycnometer; the reported values are

corrected to 0°C and should be accurate in most cases to ±0.03. Refractive indices were measured by the dispersion method at room-temperature and are considered accurate to ±0.002. For extinction angles of the amphiboles, see below. The anorthite content of the coexisting plagioclase was determined by the symmetrical extinction method, supplemented by refractive indices in a few cases, but in rocks 528, 337, 193 and 647 the plagioclase was analyzed by microprobe. The An contents in the analyzed samples closely agree with those optically determined.

Chemical analyses were carried out by combining classical and modern methods, using suitable laboratory standards for reference. SiO₂ was determined gravimetrically; FeO by titration (Wilson, 1955); TiO₂ and P₂O₅ colorimetrically, following Riley (1958) and using a Unicam SP600 series-2 spectrophotometer. H₂O was determined by the Penfield method (see below for details) and F by the rapid method of Hall and Walsh (1969). The remaining elements were determined by atomic absorption, using emission flame photometric methods for the alkalis. All the determinations except SiO₂ were duplicated and the reported values for the major elements should be accurate to ±1% of the amounts present.

Physical properties of the amphiboles

Refractive indices, birefringence, and 2V

The influence of Ti, Fe³⁺ and Fe²⁺ on the optical properties, especially refractive indices, has been elaborated by many workers since the beginning of this century. Profi *et al.* (1974) suggested that γ increases and 2V decreases as Fe and Ca in amphibole increase. Deer *et al.* (1963) and Binns (1965b) showed that RI increases as Fe substitution for Mg increases. However, a considerable scatter is seen in their data and this has been attributed to other substitutions, notably Al^{iv} for Si and Al^{vi} for R²⁺ octahedrally coordinated cations, the former being similar and the latter opposite in effect to the Fe for Mg substitution. The effect of reducing RI by substitution of Mg and Al^{vi} in octahedrally coordinated sites was clarified by Rosenzweig and Watson (1954) and Bilgrami (1964) who found a good negative correlation between RI and (Mg + Al^{vi})/($\Sigma M_1 + M_2 + M_3$) ratios for hornblendes from the Pennsylvanian Piedmont and Hindubagh (Pakistan), respectively.

To study the influence of composition, several possibilities were explored by plotting RI against various simple and complex atomic ratios. While the findings cited above are substantiated by this work, the best correlation here (*i.e.*, that with minimum scatter) is obtained when RI is plotted against $100(\text{Mg} + \text{Al}^{\text{vi}})/(\text{Mg} + \text{Al}^{\text{vi}} + \text{Al}^{\text{iv}} + \text{Ti} + \text{Fe}^{\text{3+}} + \text{Fe}^{\text{2+}} + \text{Mn})$. These data (Fig. 1) thus confirm that RI and $2V$ variation is a function of complex substitutions and therefore cannot be used in determining even the principal substitutions ($\text{Mg} \rightleftharpoons \text{Fe}^{\text{2+}}$; $\text{Si} \rightleftharpoons \text{Al}$) in hornblendic amphiboles.

Optic axial angles were not determined on a universal stage, but the values computed from RI show a general decrease with decrease in the above ratio, as also suggested by the work of Binns (1965b) and Profi *et al.* (1974) for the Mg/Fe ratio. It is worth noting that $2V$ shows a gentle decline as the ratio decreases to 50 and a rapid fall with further lowering of this ratio.

Density

The density of hornblendes has been shown to increase with Fe content (Deer *et al.* 1963; Binns, 1965b). We found an increase in density with decreasing $\text{Mg}/(\text{Mg} + \text{Fe}^{\text{2+}} + \text{Fe}^{\text{3+}} + \text{Mn})$, $100(\text{Mg} + \text{Al}^{\text{vi}})/(\text{Al}^{\text{vi}} + \text{Mg} + \text{Fe}^{\text{2+}} + \text{Fe}^{\text{3+}} + \text{Ti} + \text{Mn})$, and $100(\text{Mg} + \text{Al}^{\text{vi}})/(\text{Al}^{\text{vi}} + \text{Al}^{\text{iv}} + \text{Mg} + \text{Fe}^{\text{2+}} + \text{Fe}^{\text{3+}} + \text{Ti} + \text{Mn})$, the latter producing the least scatter. (Fig. 1).

Extinction angle

Values of maximum $Z:c$ angles were determined on crushed grains as well as thin sections without using the universal stage. Deer *et al.* (1963) and Buddington and Leonard (1953) have pointed out the problems concerning accurate determination of $Z:c$. Although at least 30 measurements were made for each sample, the report values may only be approximate. In general, these amphiboles have high $Z:c$ values. Plots of $Z:c$ against various atoms in the analyses suggest an apparent but not well-defined increase in the extinction angle as $\text{Fe}^{\text{3+}}$, Ca, and $(\text{Ca} + \text{Fe}^{\text{3+}} + \text{Mn} + \text{Na})$ increase, a comparatively better correlation seen between the angle and $\text{Ca} + \text{Fe}^{\text{3+}}$ (Fig. 2). The scattering of data may at least be partly due to lack of sufficient accuracy in measurement of the angle. Bilgrami (1964) reported a decrease in $Z:c$ with increase in $\text{Fe}^{\text{3+}} + \text{Ti}$ for hornblendes from Hindubagh but the present work does not substantiate this relation.

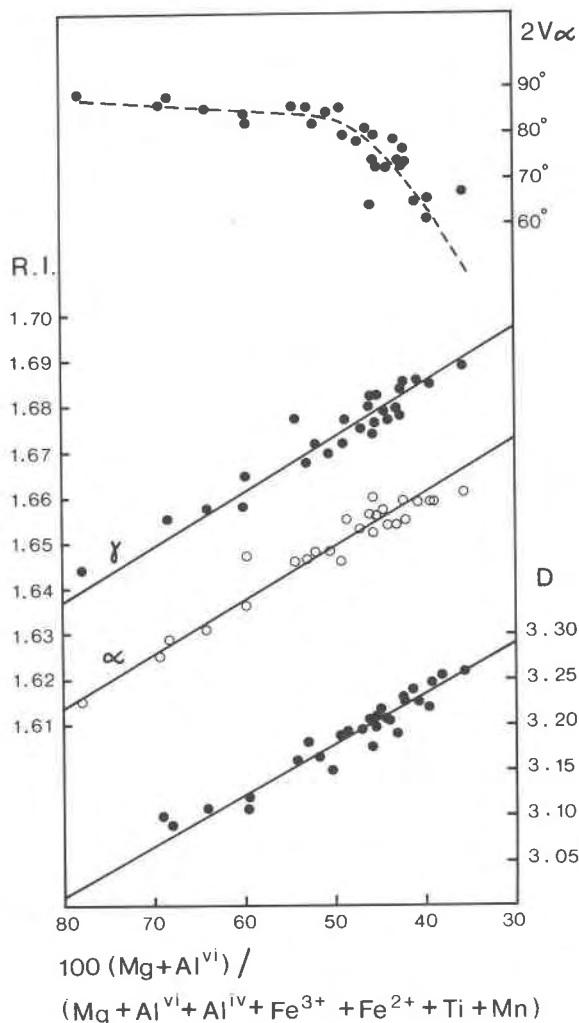


Fig. 1. Relation between the refractive indices, birefringence, $2V$, density, and $100(\text{Mg} + \text{Al}^{\text{vi}})/(\text{Mg} + \text{Al}^{\text{vi}} + \text{Al}^{\text{iv}} + \text{Ti} + \text{Fe}^{\text{3+}} + \text{Fe}^{\text{2+}} + \text{Mn})$ in Swat-Kohistan hornblendes.

Color and pleochroism

Absorption colors in amphiboles have received a good deal of attention and it has been pointed out by a number of workers that Ti and $\text{Fe}^{\text{3+}}$ play a principal role in hornblende colors. Bilgrami (1964) noted that with an increase in the $\text{Fe}^{\text{2+}}/(\text{Fe}^{\text{3+}} + \text{Ti})$ ratio in hornblendes the Z color changes from brown to green. Binns (1965b) found that in the Willyama hornblende the high Ti content accompanied by low $\text{Fe}^{\text{3+}}$ was correlated with red-brown color along Z , while the reverse situation resulted in blue-green color in that direction. This latter conclusion is also supported by data presented here. Binns also found that an increase in total content of $\text{Fe}^{\text{2+}} + \text{Ti}$ is accompanied by deeper colors and also

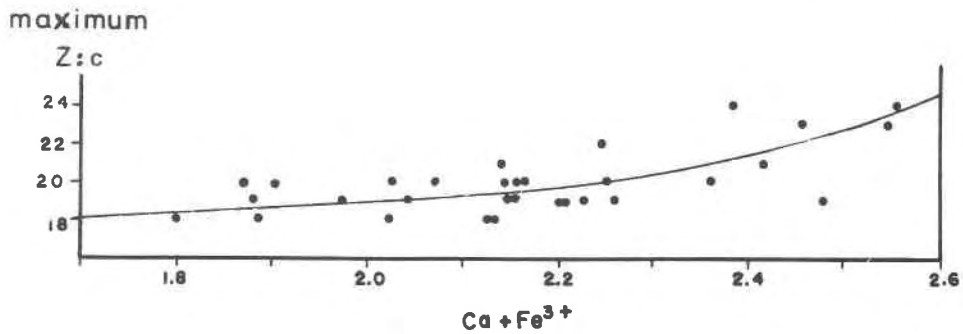


Fig. 2. Dependence of $Z:c$ on $Fe^{3+} + Ca$ in the hornblendes.

by higher occupancy of the A-site, particularly by K. Davidson (1971), similarly, reported that Fe^{3+} and Ti (and Mg values) play the principal role in colors of hornblendes from Quairading, Western Australia; Dekker (1978) pointed out that brown Z amphiboles from Rogaland have more Ti, alkalis and Al, and green amphibolite facies hornblendes have more Mn, Si, and Fe^{3+} .

The Swat-Kohistan calcic amphiboles display a variety of colors and amounts of absorption. Absorption along α is always the weakest while the maximum absorption takes place either along Z or Y. The Z colors of the amphiboles can broadly be classified into (a) blue-green, (b) green, and (c) brown, brownish green or olive. A plot of Fe^{3+} against Ti (Fig. 3) splits the amphiboles into corresponding fields such that those with the type-(c) colors have Fe^{3+}/Ti ratios of <3.0 (except sample 355 with a ratio of 4.0), while the other two types have Fe^{3+}/Ti ratios of >3.0 (except one sample); the slope of the solid line $AB'A' = 2.14$. The latter are further subdivided on the basis of Ti: amphiboles with Z blue-green have $Ti < 0.145$ and those with Z green have $Ti > 0.145$. These divisions are quite consistent with the division of the amphiboles according to their paragenesis: the blue-green Z amphiboles belong to amphibolite facies rocks (except 291), the green Z amphiboles to diorites (except 462), and those with Z brown, olive or brown-green to pyroxene- and garnet-granulites (except 355 and Q1 from amphibolites, and 647 from diorite or "retrograde" granulite; see Fig. 3).

The depth of absorption for the amphiboles can be divided into weak, moderate, and strong categories. As can be seen from the data in Appendix 1, the depth of absorption, in general, increases as $Fe^{3+} + Ti$ and Fe^{2+}/Mg increase. It is significant that Z colors in the Swat-Kohistan hornblendes are brownish even when their Ti content is low, provid-

ed that their Fe^{3+}/Ti ratio is less than 3.0. Such amphiboles, because of their low Fe^{3+} , Ti, and Fe^{2+} contents, however, are very pale along Z. Other components such as Mg and Mn and especially Al^{IV} and Al^{VI} , might exert a considerable influence on the color scheme of hornblendes.

Kostyuk and Sobolev (1969) demonstrated that calcic amphiboles from greenschist, amphibolite, and granulite facies rocks plot along separate trends on a Z vs. $f [f = 100(Fe^{2+} + Mn + Fe^{3+})/(Fe^{2+} + Fe^{3+} + Mn + Mg)]$ diagram. Such a distinction, however, is not observed here and amphiboles from

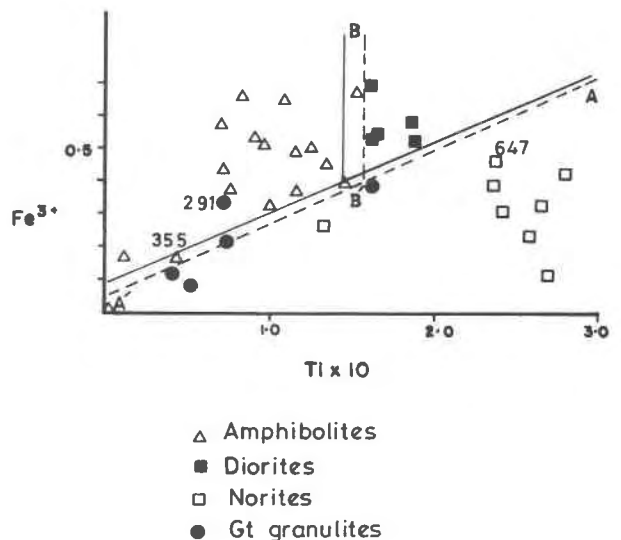


Fig. 3. Fe^{3+} vs. $Ti \times 10$ plot for the hornblendes. Those with Z = brown, brown-green, and olive have $Fe^{3+}/Ti < 3.0$ (except 355) and fall below solid line $AB'A'$. The bluish green Z amphiboles have $Fe^{3+}/Ti > 3.0$ and $Ti < 0.145$ and plot in the area defined by solid lines $BB'A'$ while the Z = green amphiboles have $Fe^{3+}/Ti > 3.0$ and $Ti > 0.145$ and plot in the area defined by solid lines $BB'A$. The dashed lines define paragenetic fields: amphiboles plotting below $AB'A'$ occur in granulites, those in the area $BB'A'$ in amphibolites and those in the area $BB'A$ in diorites.

the amphibolites, pyroxene granulites, and garnet granulites straddle the Kostyuk and Sobolev trends of granulite and amphibolite facies.

Chemistry of the amphiboles

General statement

Chemical analyses of the amphiboles from Swat-Kohistan are presented in Table 1. Analysis (b) is taken from Kemp and Leake (1975) and (a), (c) and (d) from Jan and Kempe (1973) and included here for the sake of completeness. The remaining 34 analyses are new. Judged on the basis of Leake's (1968) criteria, 28 of the new "wet" analyses appear to be of high accuracy. Analyses (a) and (d) have abnormally low H_2O^+ contents. Analysis 217 fulfills the requirements of a good analysis except for its slightly higher than 100.6% total. Analyses 104b, 528, 193 and 337 are by microprobe and for 297b there was insufficient material for an H_2O determination; the latter analysis is otherwise good. These five analyses, along with (a) and (d), have been recalculated on the basis of 23(O). Careful determination of H_2O and F in the remaining analyses allowed them to be recast on a 24(O,OH,F) rather than on a 23(O) basis.

The analyzed amphiboles are calcic and can broadly be classified as hornblendes. On Al^{iv} vs. (Na + K) and Al^{iv} vs. ($Al^{vi} + Fe^{3+} + Ti$) diagrams (adapted from Deer *et al.*, 1963) they occupy an area between tschermakite and pargasite end-members and hornblendes (Fig. 4A and 4B). Robinson *et al.* (1971) plotted the A-site occupancy against Al^{iv} and Hietanen (1974) plotted Al^{iv} against (Na + K) for a large number of amphiboles. The plot of the Al^{iv} vs. (Na + K) for the Swat-Kohistan amphiboles is remarkably similar to these two plots with the $Al^{iv}:(Na + K)$ ratio at about 3:1. Only four analyses plot away from this trend, two of them are from garnet granulites (289, 291) and two from the amphibolites (23, 347). The Al^{iv} vs. $Al^{vi} + Fe^{3+} + Ti$ plot, although showing a greater scatter, exhibits the general trend of amphiboles from the northern Sierra Nevada (Hietanen, 1974). Names according to the I.M.A. classification (Leake, 1978) are given in Appendix 1.

The total of $M_1 + M_2 + M_3$ positions in the C site is only slightly less than 5.00 in analyses 289, 2211, 713, 525, 639, 12, 4, 462, and 23. Although Cr and Ni in 12, and V (along with Cr in 462 and Zn in 525) in the remaining of these analyses are sufficient to fill this deficiency in most cases, it is still not clear

whether this discrepancy is due to analytical inaccuracy. The two M_4 positions in the B site of the Swat-Kohistan amphiboles are principally occupied by Ca (83% to 95%, with a slightly lower value of 73% in analysis 291). The remaining M_4 positions are occupied partly by Na and partly by bivalent cations in 27 analyses. The A site is occupied by (Na + K).

Figure 5 is a plot for the ionic charge balance of the amphiboles, assuming an ideal formula where $(OH + F) = 2.0$. Most of the analyses plot on a line with a slope of 1, lending support for the concept that the deficiency of charges produced by Al^{iv} for Si and Na for Ca (in B) replacement is compensated by Al^{vi} , Fe^{3+} , Ti, substitution in the C site and (Na + K) in the A site and excess OH (a deficiency of OH, on the other hand, may be compensated by additional replacement of the high valency cations in C or by higher occupancy of A). Only three analyses have significantly more charge than required by Al^{iv} and $(Na)_B$. These happen to be the analyses (12, 639, 462) with rather high Fe^{3+} and an over-estimation of this element (due to an under-estimation of FeO) can be a possible cause. The reason for Q1 plotting above the line is not clear.

It is interesting that most of the analyses with $C < 5.0$ fall slightly below this line. It cannot be ascertained whether there is a slight over-estimation of Fe_2O_3 in all of these analyses or whether there is some Ca substitution in the C site; when the C site is brought up to 5.00 by the addition of Ca, sufficient Na is transferred from the A to B sites to balance the excess charge in these analyses, including analysis 462.

The analyses of the amphiboles from the four groups of rocks do not reveal substantial differences (see below for details). Fe_2O_3 is higher in those from diorites (4.92% average Fe_2O_3) and amphibolites (3.77%) than in the amphiboles from pyroxene granulites (2.63%) and garnet granulites (2.09%). The average content of $(Na + K)_A$ of the amphiboles shows a positive correlation with the estimated temperatures for the host rocks and that of Mn negative relation: pyroxene granulites $A = 0.53$, $Mn = 0.02$; garnet granulites $A = 0.45$, $Mn = 0.01$ (the low Mn here reflecting also the paucity of host rocks in this element); amphibolites $A = 0.41$, $Mn = 0.03$; diorites $A = 0.37$, $Mn = 0.05$. The average Ti content of the amphiboles is 0.24 in the pyroxene granulites, 0.18 in diorites, 0.09 in amphibolites and 0.08 in garnet granulites. The rather high Ti content of the "retrograde" granulite amphibole 647 might

Table 1. Chemical analyses and physical properties of Swat-Kohistan hornblendic amphiboles

	SI 283	SI 297b	SI 104b	SI 289	SI 291	US 24	SI 192	SK 528	SI 217
SiO ₂	47.25	49.19	44.60	40.98	44.58	44.09	43.06	41.08	42.13
TiO ₂	0.39	0.49	0.69	1.47	0.66	2.35	2.37	2.34	2.50
Al ₂ O ₃	13.20	9.91	13.98	16.33	15.46	12.14	11.68	13.12	13.46
Fe ₂ O ₃	1.14	0.68	-	3.46	3.09	2.14	2.96	-	3.82
FeO	4.14	5.85	8.95*	8.33	9.50	7.35	11.33	12.86*	12.23
MnO	0.03	0.04	0.09	0.06	0.09	0.13	0.13	0.09	0.12
MgO	17.28	18.11	14.28	12.26	11.43	15.00	12.16	10.76	10.45
CaO	12.40	12.07	12.47	11.36	9.49	11.66	11.59	11.05	11.25
Na ₂ O	1.68	1.38	1.70	2.90	3.21	1.86	1.06	1.14	1.82
K ₂ O	0.06	0.01	0.00	0.31	0.22	0.44	1.44	2.34	1.24
H ₂ O ⁺	2.32	-	-	2.28	2.08	1.63	2.10	-	1.70
P ₂ O ₅	0.03	0.00	-	0.00	0.02	0.00	0.01	0.00	0.01
F	0.00	0.19	-	0.06	0.00	0.28	0.29	-	0.19
-O = F	-	0.08	-	0.02	-	0.11	0.12	-	0.08
Total	99.92	97.84	96.92	99.78	99.83	*99.86†	100.06	95.38	100.84
α	1.628	1.625	-	1.655	1.646	1.646	1.656	-	-
β	1.642	1.638	-	1.668	1.658	1.663	1.673	-	-
γ	1.655	1.650	-	1.677	1.668	1.677	1.682	-	-
Zrc	19°	18°	-	19°	18°	19°	19°	20°	-
D	3.089	3.100	-	3.191	3.180	3.158	-	-	3.237
2V _c (calc)	87°	86°	-	79°	85°	85°	72°	-	-
Numbers of ions on the basis of 24 (O, OH, F)									
Si	6.607	6.915	6.486	5.956	6.430	6.385	6.331	6.233	6.216
Al	1.393	1.085	1.514	2.044	1.570	1.615	1.669	1.767	1.784
Al	0.783	0.557	0.776	0.754	1.059	0.458	0.356	0.687	0.557
Ti	0.041	0.051	0.075	0.161	0.072	0.256	0.262	0.267	0.278
Fe ³⁺	0.119	0.073	0.228	0.379	0.335	0.233	0.327	0.106	0.424
Fe ²⁺	0.484	0.688	0.831	1.012	1.146	0.990	1.393	1.526	1.509
Mn	0.003	0.005	0.011	0.007	0.011	0.016	0.016	0.012	0.015
Mg	3.601	3.798	3.087	2.656	2.457	3.237	2.666	2.433	2.298
Ca	1.858	1.818	1.937	1.769	1.466	1.809	1.826	1.796	1.779
Na	0.455	0.377	0.478	0.817	0.898	0.522	0.302	0.335	0.521
K	0.010	0.002	-	0.058	0.040	0.082	0.270	0.453	0.234
OH	2.164	-	-	2.211	2.002	1.575	2.060	-	1.674
F	-	-	-	0.028	-	0.128	0.135	-	0.089
T	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
C	5.000	5.000	5.000	4.969	5.000	5.000	5.000	5.000	5.000
B	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
A	0.354	0.369	0.419	0.644	0.484	0.606	0.417	0.615	0.615
mg [*]	85.60	83.22	74.39	65.52	62.22	73.97	60.55	59.63	54.12
mg ^{**}	88.15	84.66	78.79	72.41	68.19	78.43	65.67	61.45	60.36
P.p.m.									
Co	88	64	-	71	65	67	80	-	66
Cr	97	238	1095	91	52	6190	333	-	111
Cu	12	17	-	11	29	12	16	-	31
Li	1	1	-	1	5	1	1	-	5
Ni	670	184	-	61	53	545	340	-	91
Pb	5	5	-	5	5	5	5	-	5
V	177	477	-	759	470	462	710	-	650
Zn	141	70	-	108	238	74	126	1125	170

Analyst: M.Q. Jan. Microprobe analyses (104b by G. Mehmet and 528 by J.-P. Bard) recalculated on a 23(O) basis.

mg* = 100 Mg/(Mg + Fe²⁺ + Fe³⁺ + Mn). mg** = 100Mg/(Mg + Fe²⁺)

Analyses 283 to 291 are of amphiboles from the Jijal garnet granulites, 24 to 217 from pyroxene granulites.

Anal. 24 includes Cr₂O₃ 0.90% (Cr 0.103 in formula).

Table 1. (continued)

	SI 193	SI 221	SI 337	SK 647	SK 705	(a)	SK 713	SK 525	SK 639
SiO ₂	41.26	43.13	40.45	43.90	45.29	45.10	45.47	43.39	42.72
TiO ₂	2.08	2.09 ⁺	1.17	2.11	1.47	1.47	1.66	1.43	1.65
Al ₂ O ₃	12.02	11.19	15.91	10.66	9.10	10.07	8.27	10.56	10.97
Fe ₂ O ₃	-	3.46	-	4.06	4.91	4.72	5.18	6.10	4.57
FeO	5.76 [*]	14.02	17.02	10.87	11.08	11.50	11.46	11.43	12.77
MnO	0.19	0.23	0.22	0.29	0.40	0.40	0.43	0.47	0.37
MgO	10.22	10.25	8.06	12.24	12.59	12.04	11.89	10.72	10.11
CaO	10.70	11.16	10.97	11.35	10.88	11.78	11.61	11.70	11.66
Na ₂ O	1.28	1.31	1.33	1.20	1.06	1.26	1.12	1.18	1.12
K ₂ O	1.73	1.16	1.65	1.22	0.74	1.12	0.79	1.03	1.33
H ₂ O ⁺	-	2.20	-	1.77	2.10	0.56	2.06	1.94	2.11
P ₂ O ₅	0.00	0.00	0.00	0.01	0.01	-	0.01	0.00	0.01
F	-	0.43	-	0.20	0.05	0.05	0.10	0.25	0.19
-O = F	-	0.18	-	0.08	0.02	0.02	0.04	0.11	0.08
TOTAL	95.24	100.45	96.78	99.80	99.66	100.05	100.01	100.09	99.50
α	-	1.659	-	1.656	1.652	1.660	1.654	1.659	1.659
β	-	1.678	-	1.670	1.668	-	1.669	1.677	1.677
γ	-	1.685	-	1.680	1.674	1.682	1.677	1.685	1.685
Z:c	20 ^o	20 ^o	20 ^o	20 ^o	19 ^o	-	21 ^o	23 ^o	24 ^o
D	-	3.245	-	3.204	3.174	-	3.203	3.226	3.220
2V _α (calc)	-	61 ^o	-	80 ^o	64 ^o	-	72 ^o	65 ^o	65 ^o
Numbers of ions on the basis of 24 (O, OH, F)									
Si	6.312	6.379	6.113	6.491	6.667	6.565	6.710	6.443	6.396
Al	1.688	1.621	1.887	1.509	1.333	1.435	1.290	1.557	1.604
Al	0.488	0.330	0.947	0.350	0.247	0.293	0.148	0.292	0.332
Ti	0.239	0.232	0.133	0.235	0.163	0.161	0.184	0.160	0.186
Fe ³⁺	0.321	0.386	0.264	0.451	0.543	0.517	0.575	0.682	0.515
Fe ²⁺	1.695	1.734	1.887	1.344	1.364	1.400	1.414	1.420	1.600
Mn	0.025	0.028	0.028	0.036	0.050	0.049	0.054	0.059	0.047
Mg	2.330	2.259	1.815	2.698	2.763	2.612	2.615	2.373	2.256
Ca	1.754	1.768	1.776	1.798	1.716	1.833	1.836	1.861	1.870
Na	0.380	0.375	0.390	0.345	0.303	0.355	0.321	0.339	0.326
K	0.338	0.186	0.318	0.231	0.140	0.208	0.149	0.195	0.254
OH	-	2.170	-	1.745	2.063	-	2.027	1.922	2.107
F	-	0.201	-	0.093	0.023	-	0.047	0.118	0.090
T	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
C	5.000	4.969	5.000	5.000	5.000	5.000	4.990	4.986	4.936
B	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
A	0.562	0.329	0.559	0.488	0.289	0.433	0.306	0.395	0.450
mg ²⁺	53.31	51.26	45.44	59.57	58.54	57.1	56.14	52.34	51.06
mg ³⁺	57.89	56.57	49.03	66.75	66.95	65.11	65.65	62.56	58.51
p.p.m.									
Co	-	76	-	65	57	-	50	55	53
Cr	684	68	137	82	82	30	74	33	113
Cu	-	33	-	16	82	-	40	26	34
Li	-	3	-	3	5	-	3	4	10
Ni	-	140	-	105	89	60	85	59	88
Pb	-	5	-	5	5	-	5	5	5
V	-	190	-	475	430	200	410	431	504
Zn	402	181	-	182	243	-	203	235	199

Analyst: M.Q. Jan. Anal. (a) from Jan and Kempe (1973) and recalculated on 23(O) basis because of low H₂O + F content. Microprobe anal. 193 and 337 by J.-P. Bard.

Analyses 193 to 337 are of amphiboles from pyroxene granulites, 647 to 639 from quartz diorites.

Table 1. (continued)

	Q1	(b)	US 12	SI 355	SI 352	US 19	SI 347	(c)	SI352b	US19A
SiO ₂	50.07	44.77	46.04	49.30	44.02	41.38	43.76	44.09	44.38	41.31
TiO ₂	0.05	0.39	0.68	0.41	0.13	1.35	1.07	0.87	0.92	1.11
Al ₂ O ₃	11.92	17.17	11.60	9.20	18.27	16.15	14.89	11.64	12.82	16.52
Fe ₂ O ₃	0.01	1.23	5.20	1.60	1.53	3.55	3.33	4.87	2.78	4.52
FeO	2.31	5.26	3.84	7.83	7.20	7.68	8.81	10.56	11.17	10.15
MnO	0.05	0.13	0.37	0.18	0.09	0.13	0.23	0.29	0.36	0.15
MgO	19.72	16.10	15.21	15.75	13.40	13.18	12.37	12.33	11.38	10.79
CaO	12.45	10.38	12.38	12.21	11.29	11.51	11.50	11.24	11.59	10.93
Na ₂ O	1.16	1.50	1.18	1.27	1.94	2.18	1.02	1.40	1.58	2.01
K ₂ O	0.12	0.37	1.15	0.05	0.33	0.42	0.17	0.39	0.74	0.26
H ₂ O ⁺	1.71	2.80	1.90	2.11	1.97	1.97	2.20	1.64	1.89	2.10
P ₂ O ₅	0.02	0.06	0.00	0.00	0.00	0.00	0.02	-	0.02	0.00
F	0.01	-	0.46	0.17	0.00	0.81	0.05	0.01	0.21	0.29
-O = F	-	-	0.19	0.07	-	0.34	0.02	-	0.09	0.12
TOTAL	100.66	100.15	99.82	100.01	100.17	99.97	99.40	100.33	99.75	100.02
α	1.615	-	1.647	1.631	1.636	1.648	1.648	-	1.646	1.654
β	1.630	-	1.657	1.645	1.648	1.660	1.661	-	1.660	1.667
γ	1.644	-	1.665	1.657	1.658	1.670	1.671	-	1.672	1.676
Z:c	20°	-	23°	20°	19°	20°	20°	-	18°	19°
D	-	-	3.118	3.108	3.110	3.149	3.166	-	3.186	3.200
2V _α (calc)	88°	-	82°	85°	84°	84°	82°	-	85°	79°
Number of ions on the basis of 24 (O, OH, F)										
Si	6.949	6.23	6.580	6.996	6.248	5.979	6.324	6.592	6.510	6.023
Al	1.051	1.77	1.420	1.004	1.752	2.021	1.676	1.408	1.490	1.977
Al	0.900	1.05	0.536	0.538	1.305	0.730	0.862	0.598	0.727	0.863
Ti	0.005	0.04	0.073	0.044	0.014	0.147	0.116	0.096	0.101	0.122
Fe ³⁺	0.001	0.13	0.560	0.171	0.164	0.386	0.363	0.536	0.307	0.496
Fe ²⁺	0.269	0.61	0.459	0.929	0.855	0.928	1.065	1.291	1.371	1.238
Mn	0.006	0.02	0.045	0.021	0.011	0.016	0.028	0.036	0.045	0.018
Mg	4.079	3.34	3.240	3.331	2.834	2.839	2.664	2.687	2.487	2.345
Ca	1.851	1.55	1.897	1.856	1.717	1.782	1.781	1.761	1.822	1.708
Na	0.312	0.40	0.327	0.349	0.534	0.611	0.287	0.397	0.449	0.568
K	0.022	0.07	0.209	0.009	0.059	0.078	0.031	0.073	0.139	0.049
OH	1.583	2.60	1.812	1.997	1.864	1.898	2.121	1.600	1.849	2.042
F	0.004	-	0.208	0.076	-	0.370	0.023	0.005	0.098	0.134
T	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
C	5.000	5.000	4.913	5.000	5.000	5.000	5.000	5.000	5.000	5.000
B	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
A	0.445	0.21	0.433	0.248	0.493	0.517	0.197	0.475	0.448	0.407
mg*	93.66	81.46	75.28	74.82	73.37	68.10	64.66	59.1	59.07	57.24
mg**	93.81	84.56	87.59	76.40	76.82	75.37	71.44	67.55	64.46	65.45
p.p.m.										
Co	31	-	117	68	64	59	53	-	48	46
Cr	500	-	774	587	38	126	601	70	385	19
Cu	40	-	18	27	18	70	8	-	17	1
Li	2	-	16	1	4	1	1	-	2	1
Ni	800	-	527	312	392	77	219	100	118	35
Pb	-	-	5	5	5	5	5	-	5	5
V	105	-	209	355	86	814	354	250	338	450
Zn	257	-	334	68	68	41	150	-	143	69

Analyst: M.Q. Jan. Anal. (b) from Kemp and Leake (1975); anal. (c) from Jan and Kempe (1973). Anal. Q1 is by R.A. Howie (inductively-coupled plasma spectrometer) and includes Cr₂O₃ 0.95, NiO 0.11% (Cr 0.104, Ni 0.012 in formula).

Analyses Q1 to 19A are of amphiboles from amphibolites and gneisses.

Table 1. (continued)

	US 4	(d)	SK 462	US 8	SI 194	SI 177	SI 369	SI 343	US 23	SI 202
SiO ₂	44.49	44.12	42.38	42.72	42.33	40.51	40.71	41.99	40.25	41.42
TiO ₂	0.75	0.80	1.37	1.20	0.88	0.83	0.66	1.05	0.68	0.96
Al ₂ O ₃	11.44	13.64	11.88	13.81	15.57	18.27	18.37	15.79	16.92	13.92
Fe ₂ O ₃	5.93	4.38	5.90	4.02	4.61	4.69	3.93	4.33	3.25	5.74
FeO	9.63	11.10	9.97	11.48	11.54	11.44	12.04	12.50	14.71	14.34
MnO	0.30	0.26	0.28	0.27	0.31	0.20	0.15	0.42	0.30	0.40
MgO	11.39	11.11	11.16	10.66	9.82	8.86	8.59	8.90	7.77	8.00
CaO	11.55	11.51	12.01	11.25	10.99	10.73	10.81	10.48	10.41	10.82
Na ₂ O	1.75	1.56	1.18	1.54	1.67	2.01	1.80	1.92	2.92	1.97
K ₂ O	0.42	0.45	1.68	0.69	0.53	0.27	0.40	0.68	0.94	0.35
H ₂ O ⁺	1.91	0.39	2.17	1.87	1.84	1.83	2.24	1.87	2.07	1.94
P ₂ O ₅	0.04	-	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.01
F	0.00	0.01	0.36	0.19	0.02	0.69	0.07	0.19	0.38	0.31
-O = F	-	-	0.15	0.08	0.01	0.29	0.03	0.08	0.16	0.13
TOTAL	99.60	99.42	100.19	99.63	100.11	100.04	99.74	100.04	100.44	100.05
α	1.653	-	1.659	1.655	1.657	1.659	1.654	1.655	-	1.661
β	1.666	-	1.675	1.670	1.671	1.675	1.669	1.673	-	1.680
γ	1.675	-	1.685	1.678	1.679	1.684	1.679	1.683	-	1.689
Z:c	19°	-	24°	19°	22°	19°	18°	21°	18°	20°
D	3.196	-	3.222	3.208	3.207	3.215	3.190	3.224	3.252	3.258
2V _α (calc)	78°	-	76°	72°	73°	73°	78°	73°	-	67°
Numbers of ions on the basis of 24 (O, OH, F)										
Si	6.550	6.394	6.258	6.311	6.226	5.942	5.976	6.201	5.987	6.201
Al	1.450	1.606	1.742	1.689	1.774	2.058	2.024	1.799	2.013	1.799
Al	0.535	0.725	0.325	0.716	0.925	1.101	1.155	0.950	0.955	0.659
Ti	0.083	0.087	0.152	0.133	0.097	0.092	0.073	0.116	0.076	0.108
Fe ³⁺	0.656	0.477	0.655	0.447	0.511	0.518	0.434	0.481	0.365	0.646
Fe ²⁺	1.185	1.346	1.232	1.418	1.420	1.403	1.478	1.544	1.830	1.296
Mn	0.037	0.032	0.035	0.033	0.039	0.025	0.019	0.052	0.038	0.050
Mg	2.499	2.399	2.456	2.347	2.153	1.936	1.879	1.959	1.722	1.785
Ca	1.822	1.787	1.901	1.780	1.732	1.686	1.701	1.659	1.659	1.735
Na	0.498	0.439	0.337	0.440	0.476	0.571	0.512	0.550	0.842	0.572
K	0.080	0.084	0.315	0.129	0.099	0.051	0.074	0.064	0.179	0.067
OH	1.875	-	2.137	1.843	1.805	1.791	2.192	1.842	2.054	1.938
F	-	-	0.168	0.088	0.010	0.320	0.033	0.089	0.179	0.147
T	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
C	4.995	5.00	4.855	5.000	5.000	5.000	5.000	5.000	4.986	5.000
B	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
A	0.400	0.376	0.553	0.443	0.452	0.383	0.325	0.375	0.680	0.418
mg*	57.09	56.4	56.10	55.29	52.22	49.87	49.32	48.54	43.54	41.73
mg**	67.83	64.09	66.59	62.34	60.26	57.98	55.97	55.92	48.48	49.47
P.P.m.										
Co	70	-	65	57	51	40	45	34	54	29
Cr	160	150	305	182	138	16	32	62	33	74
Cu	7	-	8	75	14	12	168	16	35	28
Li	3	-	4	6	9	4	5	2	7	7
Ni	86	100	180	128	80	16	41	31	28	44
Pb	5	-	5	5	5	5	41	5	5	5
V	418	400	513	479	470	538	376	352	513	323
Zn	154	-	160	168	204	156	181	203	181	176

Analyst: M.Q. Jan. Anal. (d) is from Jan and Kempe (1973), and includes H₂O⁺ 0.09%, and is recalculated on 23(O) basis.

Analyses 4 to 202 are of amphiboles from amphibolites and gneisses.

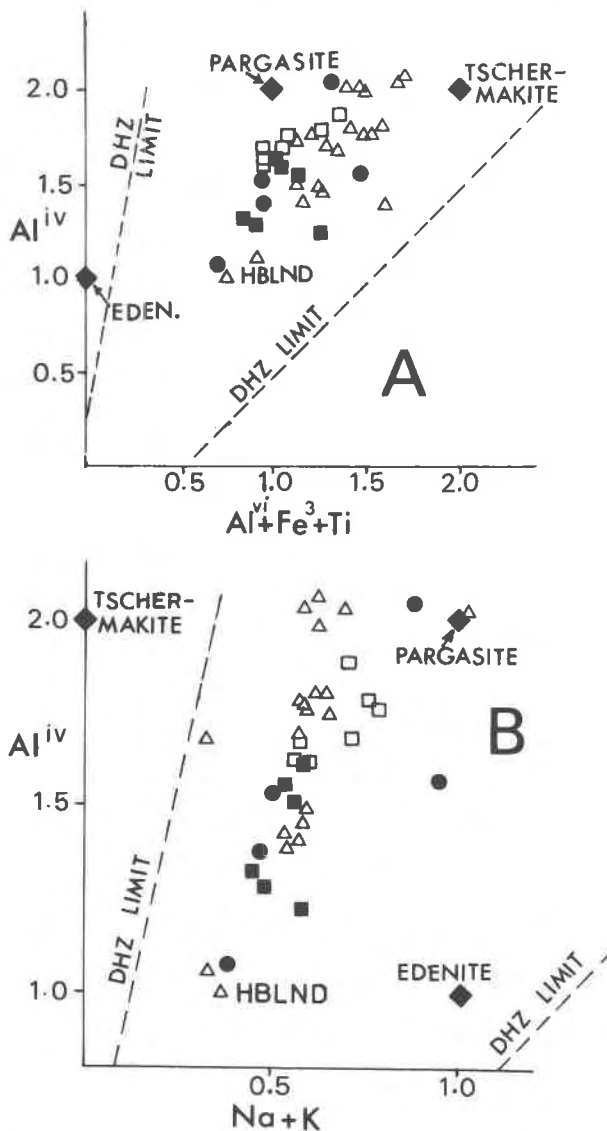


Fig. 4. Plots of Al^{iv} vs. $Al^{vi} + Fe^{3+} + Ti$ (A) and Al^{iv} vs. $Na + K$ (B) in one-half unit cell of the Swat-Kohistan hornblendes (adapted from Deer, Howie, and Zussman, 1963). Circles: garnet granulites; open squares: pyroxene granulites; filled squares: quartz diorites; open triangles: amphibolites and gneisses.

suggest that the well-formed amphibole in this rock developed during the waning stages of granulite facies conditions.

Trace element contents in the amphibole analyses do not show systematic variation in all cases because of the diversity of bulk chemistry and mineralogy of the host rocks. However, Co values are steady whereas Ni shows a general decrease and Zn an increase with reduction in mg^* . Li also appears to be higher in the Fe-rich amphiboles which is not

surprising. The abnormally high Cr content of US 24 is due to the high Cr content (3400 ppm) of its host rock which contains no chromian spinel.

The analyzed amphiboles are broadly similar to other amphiboles described from granulites, amphibolites, and diorites (Deer *et al.*, 1963) and no purpose will be served in presenting experimental data concerning the stability of such amphiboles. It is now well-known that in water-rich environment hornblendic amphiboles are stable in high $P-T$ conditions. A summary of the experimental work concerning pargasite and tschermakite has been given by Bunch and Okrusch (1973). More recently Mysen and Boettcher (1975), in their experiments on garnet websterite + H_2O at high pressures and temperatures, found that amphiboles are enriched in the tschermakite component at higher temperature while the pargasite content increases with increasing pressure.

Chemicographic relations

The various constituents of the amphibole analyses were plotted against each other and against those of their host rocks (Table 2¹) in order to evaluate possible correlations and the influence of bulk chemistry on that of the amphiboles. Only some of the diagrams selected from a great number are presented here.

Ionic relations in the amphibole analyses. In the amphibole analyses, an inverse relationship is noted in the quantities of Si and Al (especially Al^{iv}); Si and ($Al^{iv} + Ti$); Mg and Fe^{2+} ; $Mg/(Mg + Fe_{total})$ and Ca and Al^{iv} ; Ca and $M_1 + M_2 + M_3$ total; OH and (A); and possibly in Fe^{3+} and Al^{vi} , and Si and Ti. A positive correlation is found between Al^{iv} and $Na + K$; Al^{vi} and Na; Al^{iv} and ($Al^{vi} + Fe^{3+} + Ti$); and Na and (A). The increase in Mn with increase in Fe is not as obvious as found for the pyroxenes of Swat-Kohistan (Jan and Howie, 1981) some of which coexist with the amphiboles. Ti shows a positive correlation with (A) and Al^{iv} when plotted for the amphiboles from the individual rock types but these relationships are not clear when the analyses are taken as a whole. Buddington and Leonard (1953) noted a decrease in (OH + F + Cl) with decrease in Mg/Fe ratio but such a relationship is not found here. Many of the above relations are in agreement with those found by other workers.

Saxena and Ekstrom (1970) found a positive

¹The authors will gladly supply a copy of Table 2 containing the rock analyses on request.

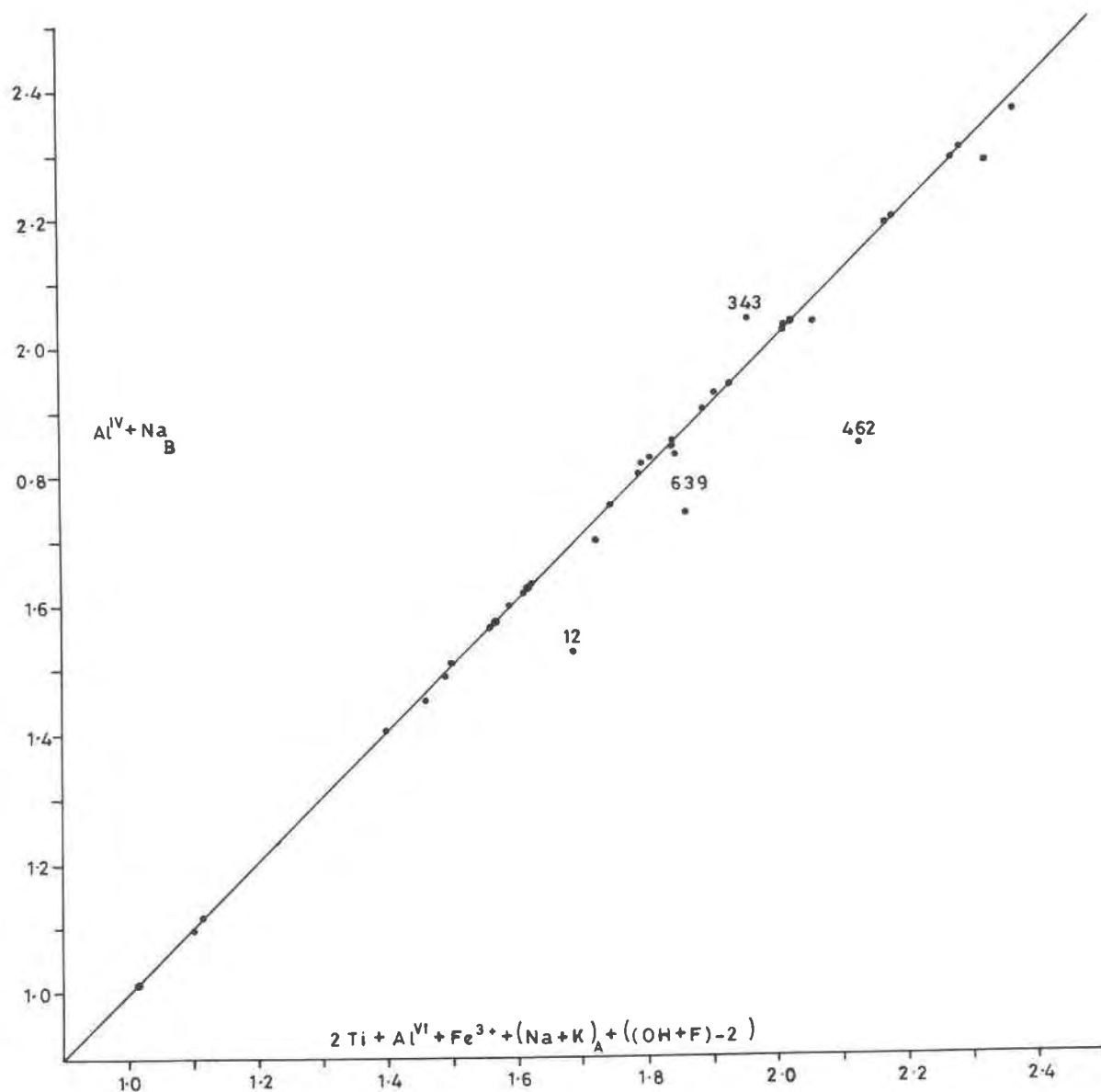


Fig. 5. Ionic charge-balance plot of the hornblendes showing that the deficiency of charges due to $Al^{IV} \rightarrow Si$ and $Na \rightarrow Ca_B$ substitution is compensated by $Al^{VI} + Fe^{3+} + Ti$ in $M1, M2, M3$ positions, $Na + K$ in A, and excess $OH + F$. (In case of $OH + F < 2.0$, additional occupancy of A site or substitution of higher valency cations in $M1-3$ positions is to be expected). Most of the analyses display this relation faithfully by plotting along the diagonal line with 1:1 slope. All amphibole analyses with no octahedral vacancies (in B) and no Ca in A-sites should fall on this line.

correlation between Fe^{2+} and Mn, OH and Ti, and a negative correlation between Fe and Mg, Na and Ca, Si and Ti, and Al^{IV} and $Ti + Fe^{3+}$. Kostyuk and Sobolev (1969) found a negative correlation between Fe^{2+} and $Mg + Al$ and $Si + Fe^{3+}$ and Al^{VI} , F and OH, and a positive correlation between K and Fe^{2+} , and Na and Al^{IV} . The significant correlation between Si and Ti was interpreted by Kostyuk and Sobolev to indicate isomorphism while the lack of

significant correlation between Na and Ca was thought to suggest a lack of diadochy between the two. In Swat-Kohistan amphiboles, a positive correlation between Na and Al^{IV} may suggest $NaAl \rightleftharpoons Si$ and $NaAl_3 \rightleftharpoons MgSi_2$ substitutions, and the smaller amount of Na (in W) compared to $Al^{VI} + Fe^{3+}$ suggests $AlAl$ or $AlFe^{3+} MgSi$ substitution (cf. Deer *et al.* 1963; Kostyuk and Sobolev, 1969; Onuki and Tanaka, 1974).

Relations between amphibole and host-rock composition. It has been suggested that the Mg/Fe ratio in amphiboles is strongly dependent upon this ratio in their host rocks (Binns, 1965a, 1965b; Zakrutkin and Grigorenko, 1967; Grapes *et al.*, 1977). However, a number of additional factors such as increasing oxygen fugacity (Bard, 1970; Hietanen, 1974), and metamorphic grade (Wenk *et al.*, 1973) have also been invoked to explain an increase in this ratio. Davidson's (1971) work does not suggest an influence of metamorphic grade upon this ratio. Gable and Smith (1975) noted that the ratio is also influenced by the Fe^{3+} content of hornblendes and of biotite when present.

These suggestions were explored and it was found that the $\text{MgO}/(\text{MgO} + \text{FeO})$ and $\text{Mg}/(\text{Mg} + \text{Fe}^{2+} + \text{Fe}^{3+} + \text{Mn})$ ratios of the hornblendes show a good positive correlation with these ratios in their host rocks (Figs. 6A and 6B). Plots of mg and $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ in hornblende against $\text{Fe}_2\text{O}_3/(\text{Fe}_2\text{O}_3 + \text{FeO})$ of their host rocks show scattering but the mg values show a general increase with oxidation ratio (*i.e.*, f_{O_2}), especially in the case of amphiboles with more than 15% Al_2O_3 .

Thus the fugacity of oxygen has some control over the mg of Swat amphiboles. This relationship is supported also by experimental work relating $\text{Mg}/(\text{Mg} + \text{Fe})$ in amphiboles to f_{O_2} (Helz, 1973; Spear, 1981). Similarly an increase in mg cannot be related to increasing temperature despite the range of P - T estimates for the four rock-types. A slight general decrease in mg is seen with increasing Al^{IV} but, as also noted by Hietanen (1974), there is considerable scatter. This work suggests that the Mg:Fe ratio in the amphiboles is principally controlled by this same ratio in the rocks but some influence is also exerted by bulk mineralogy and, to a minor extent, possibly Al^{IV} .

The $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$ ratio of the amphiboles, despite considerable scatter, shows an increase with increase in the same ratio in their host rocks and confirms the positive correlation reported between the two by Morteani (1978). The Ca and Na contents of the amphiboles are independent of bulk chemistry.

The variations in the Ca content and $\text{Ca}/(\text{Ca} + \text{Na})$ ratio of the host rocks are principally expressed in plagioclase and that their influence over amphibole composition is negligible has been suggested by Grapes *et al.* (1977) and Onuki and Tagiri (1972). While this may be so in rocks essentially composed of hornblende and plagioclase, the conclusion may

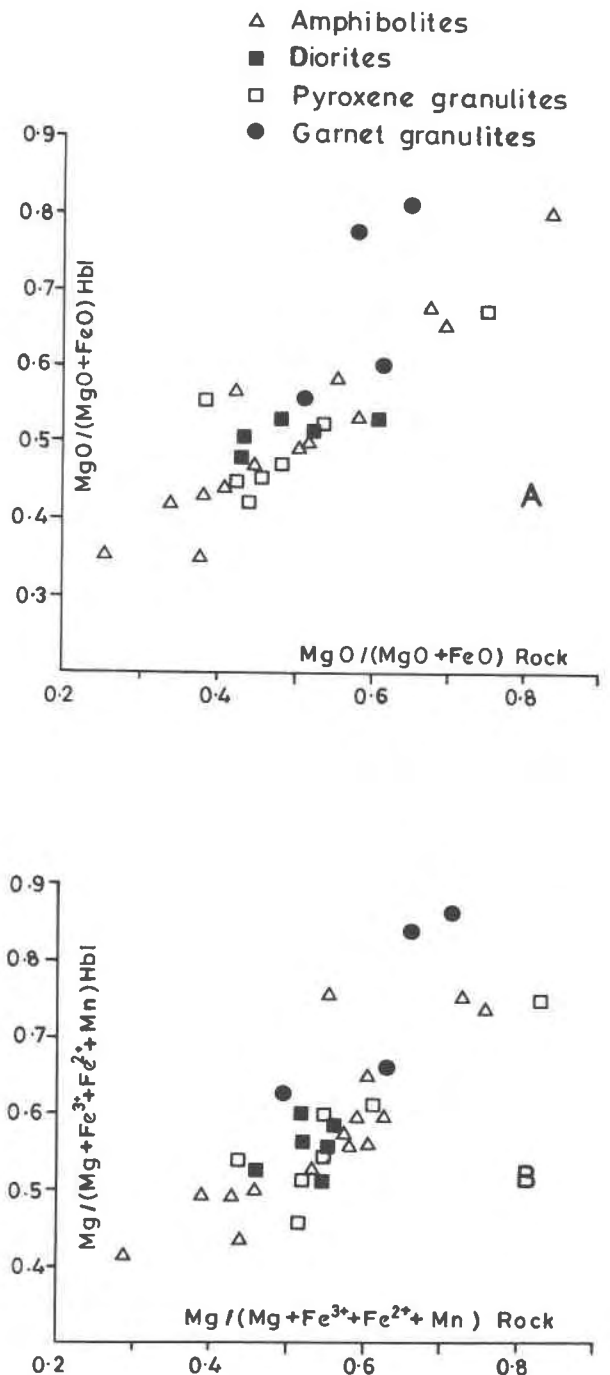


Fig. 6. Plots of $\text{MgO}/(\text{MgO} + \text{FeO})$ (A), and $\text{Mg}/(\text{Mg} + \text{Fe}^{2+} + \text{Fe}^{3+} + \text{Mn})$ (B) of the hornblendes against their host rocks suggesting the Mg/Fe dependence of the hornblendes upon bulk composition.

not be valid in the case of polymineralic rocks containing appreciable amounts of other calcic minerals. Plots of $100\text{CaO}/(\text{CaO} + \text{Na}_2\text{O})$ in host rocks vs. amphiboles and the anorthite content of the

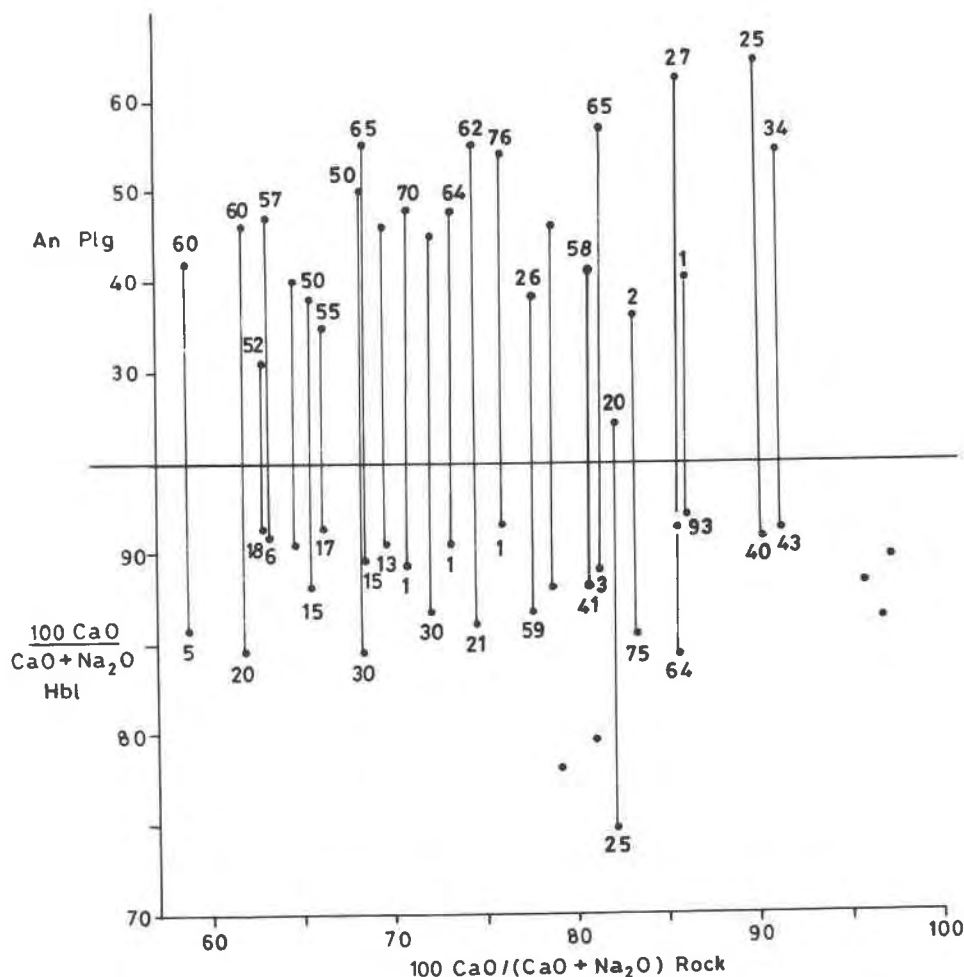


Fig. 7. Plot of $100 \text{ CaO}/(\text{CaO}+\text{Na}_2\text{O})$ of host rocks vs. this ratio in the hornblendes and anorthite content of the coexisting plagioclase, demonstrating that neither the Ca content in the amphiboles nor in plagioclase is a strict function of bulk chemistry. Tie-lines are drawn between coexisting pairs. Numbers at the ends of the tie-lines indicate modal percentages of plagioclase and hornblende.

plagioclase (Fig. 7), and of CaO content of host rock vs. CaO in hornblende and An in plagioclase demonstrate that neither the Ca in amphibole nor the Ca in plagioclase is a strict function of bulk chemistry. Clearly, the composition and proportion of all the calcic minerals (plagioclase, amphibole, garnet, epidote, sphene, clinopyroxene, and calcite) have influenced the calcium content of the amphiboles and plagioclase.

Deer (1938) and Bilgrami (1964) found a close relation between the silica content of hornblendes and their host rocks but such is not the case here. The rather low SiO_2 content of some of the amphiboles in "silica-saturated" (quartz-bearing) rocks (e.g., 528, 193, 337, 194, 363, 343, 202) might be of petrogenetic significance and merits further investigation.

Relations between amphibole and other mafic minerals. Other minerals such as orthopyroxene, clinopyroxene, garnet, epidote, and biotite which coexist with amphibole in many of the Swat-Kohistan rocks were also chemically analyzed (Jan, 1977). These analyses show that among the ferromagnesian minerals the amphiboles contain most Na, K, Ti, and Ni (except for biotite) and are relatively rich in Co, V, and Zn (after biotite and orthopyroxene), richest in Cr, and poorest in Li. The Fe^{2+}/Mg ratios of coexisting orthopyroxene, clinopyroxenes, and garnets are compared with this ratio for the analyzed amphiboles in Figure 8. The data are insufficient for statistical conclusions to be drawn, but the Fe^{2+}/Mg ratios for coexisting phases of the garnet granulites can be distinguished from those of the pyroxene granulites.

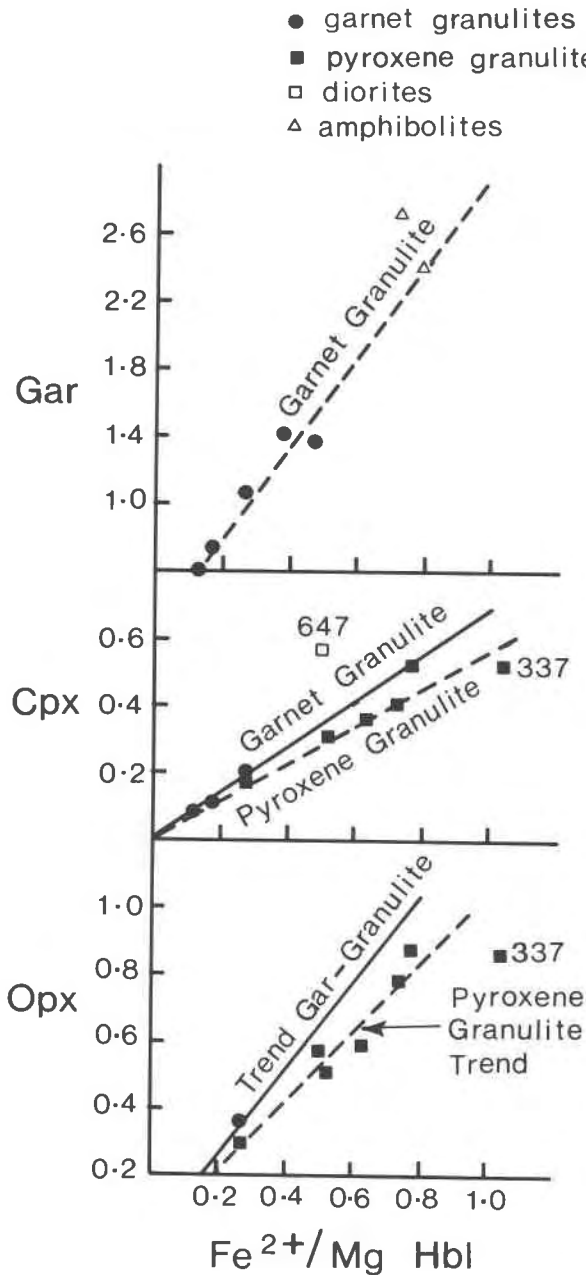


Fig. 8. Fe^{2+}/Mg ratios for analysed amphiboles plotted against Fe^{2+}/Mg in coexisting orthopyroxenes, clinopyroxenes and garnets.

H₂O and F contents of the amphiboles

The H_2O^+ content has been carefully determined to allow the recalculation of the analyses on the basis of $24(\text{O}, \text{OH}, \text{F})$ rather than on $23(\text{O})$. Leake (1968) has pointed out the difficulties concerning the determination of water and has laid stress on accu-

rate determination of this component. Kemp and Leake (1975) have discussed the significance of high water content in amphiboles, and Saxena and Ekstrom (1970) have pointed out the importance of (OH) variation in influencing the total chemical composition of amphiboles. Water was determined by the Penfield method, heating about one gram of amphibole in a silica Vitrosil tube by oxygen-natural gas flame.

The expulsion of water took place in two stages. Approximately half of it was released by heating the tube with a flame of about 900° to 1000°C and the remaining half was released from the same material when heated by a flame at about 1200°C . All the determinations were duplicated with the higher temperature flame and, in a few cases, where the difference was more than 10%, a third determination was made. The determinations were verified against a standard (BL 3571, $\text{H}_2 = 3.34\%$) kindly provided by Professor B. E. Leake.

Analyses 221, (b), 19, and 462 are worth noting for their considerably higher (OH+F) content (2.37, 2.60, 2.27, and 2.31 respectively) than the usual (OH)₂ group per half unit cell. The low $(\text{Na}+\text{K})_A$ occupancy (0.21) of analysis (b) has been considered by Kemp and Leake (1975) to be due to its extremely high (OH) value but also, to a small extent, the rather low Ca. The occurrence of excess water above the usual amount in the formula has not yet been satisfactorily explained; suggestions range from occupancy of the A site by H_3O^+ to minor replacement of some of the O^{2-} ions of the Si_4O_{11} chains by OH^- ions (Deer *et al.*, 1963). "Wherever the extra water is located, it enables the replacement of Si by Al^{IV} to proceed without the charge balance having to be entirely satisfied by Al^{VI} , Fe^{3+} , Ti and $(\text{Na}+\text{K})_A$ substitution and re-emphasizes the extra flexibility in substitutions in amphiboles, which calculations of the cell contents on the basis of $23(\text{O})$ do not allow" (Kemp and Leake, 1975). This suggestion holds true for the Swat-Kohistan amphiboles also, where $(\text{Na}+\text{K})_A$ shows an inverse correlation with (OH).

It has been suggested by some workers that the water content in the granulite facies amphiboles is lower than in those of the amphibolite facies. Dobretsov *et al.*'s (1972) average values of OH in hornblendes from the two facies, similarly, display a distinct difference. Such a difference, however, is not obvious in Swat-Kohistan; the average $\text{H}_2\text{O}\%$ (1.91) of the granulite amphiboles is only slightly lower than that (1.97) in the amphibolite amphiboles

while the average value (2.23) in the amphiboles of the garnet granulites is distinctly higher.

The amphiboles are conspicuously poor in fluorine. Only six analyses contain more than 0.3% F, the average F content being 0.19%. In most analyses the sum of $F + OH = 2$ and an underestimation of F does not seem to be the reason for the low F values. Because F has a much stronger affinity for Mg than for Fe (Cameron and Gibbs, 1973), it is expected that the F content will increase with increasing Mg/Fe ratio of amphiboles. However, such a relationship is not seen in the Swat-Kohistan hornblendes. A plot of Mg values against F in hornblendes from six different areas (Kanisawa *et al.* 1979) is similarly inconclusive.

In the dehydration process of hydrous minerals during progressive metamorphism, fluorine tends to remain selectively in the crystal structure of hydrous minerals so that the F content of granulite facies amphiboles is higher than those from the amphibolite facies (*cf.* Kanisawa *et al.*, 1979). The replacement of OH by F was found to raise significantly the upper stability limit of tremolite (Troll and Gilbert, 1972) and this has been correlated by some workers with stable coexistence of F-rich hornblendes in granulite facies rocks. The average F content in Swat-Kohistan amphiboles is 0.30% in pyroxene granulites, 0.23% in amphibolites, 0.14% in diorites, and only 0.06% in garnet granulites (the latter might be reflecting the paucity of the host rocks in this element). Although these values show a positive relation with temperature estimates for the rocks, the individual analyses are inconclusive. The much higher values of F in some of the amphibolite amphiboles (177, 462, 23, 12, 19) compared to the granulite facies amphiboles casts doubt on the strict dependence of F on temperature. Similarly, a plot of F against the H_2O content of the amphiboles is chaotic rather than showing an inverse relation. Therefore it cannot be suggested here that the additional entry of F is necessarily linked with the dehydration process during progressive metamorphism. Similarly, the average analyses of Dobretsov *et al.* (1972), as mentioned, contain significantly higher OH in granulite facies than in amphibolite facies amphiboles; however, the F content is approximately the same.

Al₂O₃ content of the amphiboles

A characteristic feature of the amphiboles from the Swat-Kohistan metamorphic rocks is their high Al_2O_3 ; twelve of the 32 amphiboles contain more

than 15% Al_2O_3 . The average Al_2O_3 content of the amphiboles from the amphibolites is 14.6%, from the garnet granulites 13.8%, pyroxene granulites 12.4%, and from the diorites 9.9%. The pyroxene granulite average is similar to that (12.4%) of the six amphiboles from the Madras charnockite series (Howie, 1955). High alumina seems to be a regional aspect of the hornblendic amphiboles from N. Pakistan. Bunch and Okrusch (1973) have described two Al-rich "pargasites" in a corundum- and spinel-bearing marble from Hunza, N. Pakistan. Amphiboles from some metabasites near Warsak, 150 km SW of Swat, are also rich in alumina (Kempe, 1978).

The quantity of Al_2O_3 in amphiboles has been related to silica activity, f_{O_2} (Neumann, 1976), and to pressure, temperature, and Al_2O_3 content of their host rocks (Fabriès, 1978). A plot of Al_2O_3 in amphibole *vs.* host rock shows a positive correlation but there is too much scatter. For example, the amphibole (369) with the highest amount of alumina is from a rock with only a moderate quantity of alumina when compared with the other amphibole-bearing host rocks. The silica activity does not seem to influence the Al_2O_3 content of the amphibole, as revealed by the plot of SiO_2 in the host rocks *vs.* Al_2O_3 in their amphiboles. Similarly, a plot of the Al_2O_3 in the amphiboles *vs.* oxidation ratio of their host rocks fails to reveal any dependence of the former upon f_{O_2} . Some influence, however, is clearly exerted over the amount of Al_2O_3 by the type and proportion of the coexisting minerals. Thus, amphiboles in the Jijal granulites are not the most aluminous despite the very high Al_2O_3 of their host rocks (Jan and Howie, 1981), because the abundant coexisting garnet takes up most of the alumina. Similarly, 355 is not very aluminous because it coexists with clinozoisite and An-rich plagioclase, and 24 with 12.1% Al_2O_3 is much more aluminous than its host rock ($Al_2O_3 = 5.3\%$) because of an abundance of associated pyroxenes that could accommodate only a limited amount of Al_2O_3 . Similarly the high Al content of 352 is a reflection of bulk mineralogy and composition: amphibole is the principal mineral in the rock containing 19.3% alumina. Thus it appears that the Al_2O_3 content of the Swat amphiboles is essentially influenced by three factors, namely rock composition, the nature of the associated minerals, and metamorphic conditions.

Increase in the amount of alumina in amphiboles with increasing grade of metamorphism has been

recorded in various parts of the world (*cf.* Deer *et al.*, 1963, p. 304; Dekker, 1978; Kuniyoshi and Liou, 1976; Spear 1976). Verhoogen (1962) suggested that Al^{IV} increases with increase in temperature and Heitanen (1974) noted a similar increase in the amphiboles close to the Feather River pluton, northern Sierra Nevada. An increase in Al^{VI} has been related to increasing pressure (Leake, 1965b; Kostyuk and Sobolev, 1969; Mottana and Edgar, 1969; Holloway and Burnham, 1972; Vitel and Fabriès, 1982). Fleet and Barnett (1978) found that Al^{VI} is also dependent on the availability of other competing octahedrally coordinated R^{3+} cations, particularly Fe^{3+} , and that Al^{IV} and Al^{VI} distribution apparently reflects paragenesis. Kostyuk and Sobolev (1969, p. 75) stated that "In regionally metamorphosed rocks typical hornblendes are stable within a temperature range of 900°–550°C. Decreasing temperatures cause a slight decrease in aluminium (mainly Al^{IV}) particularly at pressures above 10 kilobars." They also noted that amphiboles are less aluminous (mainly due to Al^{IV}) in the amphibolite than in the granulite-facies rocks.

In Swat-Kohistan, however, amphiboles from the amphibolite facies rocks are more aluminous than those of the granulites. The average values for the various rocks are: amphibolites Al^{IV} 1.60, Al^{VI} 0.80; Jijal granulites Al^{IV} 1.52, Al^{VI} 0.78; pyroxene granulites Al^{IV} 1.72, Al^{VI} 0.57; and diorites Al^{IV} 1.45, Al^{VI} 0.28. Binns (1965b) and Davidson (1971) also found lower Al^{VI} for the hornblendes in the granulites than in amphibolites from Western Australia. The reason for the lower Al in the amphiboles of the Jijal granulites and pyroxene granulites seems to be the abundance of the coexisting Al-rich minerals, namely garnet and plagioclase respectively. One of the Jijal amphiboles (289) is much more aluminous and also has significantly more TiO_2 and Fe_2O_3 ; Al^{VI} thus does not differ much from that of other amphiboles of garnet granulites, most of the excess Al being accommodated as Al^{IV} . Similarly SI337 has more Al than the rest of the pyroxene granulite amphiboles partly because of the lower modal plagioclase in its host rock.

A straightforward plot of Al^{VI} against Al^{IV} fails to distinguish the limits for the truly tschermakitic substitutions ($Al^{VI}, Al^{IV} \rightarrow Mg, Si$). Amphiboles which undergo glaucophane-type substitutions, $Na(M4)Al^{VI} \rightarrow Ca, Mg$, would tend to shift points above the limiting line of Leake (1965b), whereas amphiboles with edenite type substitutions, $Na(A), Al^{IV} \rightarrow \square, Si$, would shift points below the line. Because

amphiboles that plot near tschermakite in the Al^{IV} vs. Al^{VI} plot (*e.g.*, "mboziite") could have total (Na+K) values ranging from 0 to 2.0, care must be taken in plotting natural amphiboles containing significant (Na+K). Thus "a better way to study the relation of Al^{VI} vs. Al^{IV} occupancy due to tschermakite-type ($Al^{VI}, Al^{IV} \rightarrow Mg, Si$) substitutions is to remove the effect of glaucophane-type substitutions" (Doolan *et al.*, 1978). In this plot, $Al^{VI} - Na(M4)$ vs. $Al^{IV} + Na(M4)$ (Fig. 9), edenite-type and glaucophane-type substitutions shift amphibole composition in a direction parallel to the abscissa, whereas tschermakite-type substitution shifts amphibole compositions in a diagonal direction. It is also interesting to note (Fig. 9) that the pyroxene-granulite amphiboles (\square) show a much greater variation in $Al^{VI} - Na(M4)$ than in $Al^{IV} + Na(M4)$, whereas the garnet-granulite amphiboles (\bullet) on the

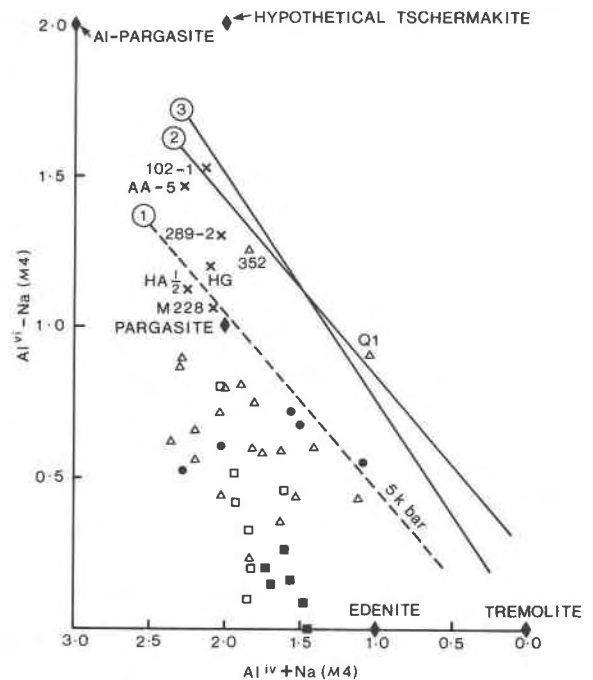


Fig. 9. $Al^{IV} + Na(M4)$ vs. $Al^{VI} - Na(M4)$ plot of the hornblendes. Also plotted are the highly aluminous amphiboles HA $\frac{1}{2}$ and AA from Hunza, Pakistan (Bunch and Okrusch, 1973) MF 228 from Lukamanier, Switzerland (Frey, 1969; Leake 1971) and 289-2 and 102-1 from Massachusetts (Doolan *et al.* 1978). Diagonal dashed line indicates an assumed pressure of 5 kbar (Raase, 1974) and lines 2 and 3 indicate maximum Al^{VI} according to Leake (1965b) and Doolan *et al.* (1978), respectively. Note the high Al^{VI} content of Q1 and 352 for their Al^{IV} values. Line 3 is based on the equation $Al^{VI} - Na(M4) = 0.75 [Al^{IV} + Na(M4)]$. Circles: garnet granulites; open squares: pyroxene granulites; filled squares: quartz diorites; open triangles: amphibolites and gneisses.

other hand, show a much greater variation in $Al^{IV} + Na(M4)$ than in $Al^{VI} - Na(M4)$ (indeed when $Ti + Fe^{3+}$ are plotted against $Al^{IV} + Na(M4)$ there is a positive correlation).

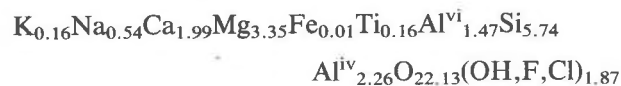
Many of the Swat metamorphic amphiboles plot near the 5 kbar line while the diorite amphiboles, as also found by Leake (1965b), plot farthest away (lowest Al^{VI}) and four of the five garnet granulite amphiboles plot above the 5 kbar line. Leake (1965a, 1965b, 1971) concluded that maximum Al^{VI} will occur in amphiboles crystallizing in highly aluminous environments with moderate or low alkali contents and under high pressures. The high Al_2O_3 content of the Swat-Kohistan metamorphic amphiboles is suggestive of high pressures, which is entirely consistent with the occurrence of garnet and rutile in the Jijal granulites and some other rocks. However, the dependence of the Al_2O_3 content of amphiboles on other factors makes it difficult to compare amphiboles from rocks of diverse mineralogy and chemistry on the basis of their Al content.

Raase (1974) reached a similar conclusion, and as an example amphiboles 352 and 352b may be examined. These two amphiboles are from outcrops only a few hundred meters apart and there is no doubt that the two have formed under similar metamorphic conditions (unless the two are faulted against each other for which there is no evidence). The Al^{IV} (1.75) and Al^{VI} (1.31) in the former are much higher than those (1.49 and 0.73 respectively) in the latter. Clearly, the alumina content of the two is a reflection of the host rock composition ($Al_2O_3 = 19.3\%$ in rock 352 and 14.6% in 352b) and bulk mineralogy (see Appendix) rather than different metamorphic conditions.

Leake (1965b, 1971) predicted that with increase in Al^{IV} in the calcic amphiboles, the amount of Al^{VI} also increases, and that $Al^{VI} \leq (0.6 \times Al^{IV}) + 0.25$; Doolan *et al.* (1975) suggest that $Al^{VI} \leq 0.7 Al^{IV} + 0.25$. Although Kostyuk and Sobolev (1969) found a negative correlation between Al^{IV} and Al^{VI} , the work of Saxena and Ekstrom (1970) suggests a positive correlation between the two. The plot of Al^{IV} vs. Al^{VI} (Fig. 9) for the Swat amphiboles supports Leake's conclusion. So far, no tschermakite end-member $[Ca(Mg,Fe^{2+})_3Al^{IV}_2Si_6Al^{VI}_2O_{22}(OH,F)_2]$ has been found in nature. Out of 1500 analyses compiled by Leake (1968, 1971), only nine gave Al^{IV} as well as $Al^{VI} > 1.3$. These, however, were discarded by Leake due to imperfect mineral separation or analyses. Frey (1969) report-

ed a highly aluminous amphibole approaching tschermakite end-member composition in rocks formed in high-pressure environments. Leake's (1971) revised analysis of this mineral contains $Al^{VI} = 1.35$ which is among the highest reliable values so far determined and is a little more than the predicted amount for an amphibole with $Al^{IV} = 1.78$. Doolan *et al.* (1978) recently described two most tschermakitic amphiboles with $Al^{IV} = 1.98$ and 1.90 and $Al^{VI} = 1.69$ and 1.42 respectively. These Al^{VI} values again are only slightly above the limits predicted by Leake and by Doolan *et al.*

Bunch and Okrusch (1973) have described two unusual amphiboles with very high Al_2O_3 contents (22.6% and 20.2%) from Hunza, N. Pakistan. In one of these of composition



the Al^{VI} is a little less than the maximum predicted amount ($Al^{VI}_{1.58}$) for an amphibole with $Al^{IV}_{2.26}$. According to Kemp and Leake (1975), this amphibole "clearly demonstrates partial substitution towards an 'end-member' not previously considered, whose composition is $(Na,K)Ca_2Mg_3Al^{IV}_2Si_5Al^{VI}_3O_{22}(OH)_2$, a subsilicic alumino-pargasite. Substitution towards such an end-member could partly explain the absence of natural samples approaching alumino-tschermakite."

Of the Swat-Kohistan amphiboles, it is notable that (b) (Kemp and Leake, 1975) and 352 have very high Al^{VI} values for their respective Al^{IV} . It may be said that among the highly aluminous amphiboles approaching tschermakite end-member, 352 is one of the most reliable analyses whose Al^{VI} of 1.305 is very near the maximum for its Al^{IV} of 1.752. Both (b) and 352, like many other Al-rich amphiboles (Leake, personal communication, 1976), are very low in Ti and Fe^{3+} .

TiO₂ content of the amphiboles

Although the TiO_2 content of the amphiboles has some dependency on the amount of titanium in the host rocks, there is a marked difference in the TiO_2 content of the amphiboles from the pyroxene granulites and amphibolites, the latter having lower Ti even when the TiO_2 content of their host rocks (*e.g.*, 177, 4) is comparable with granulites. Amphiboles in the Jijal granulites are typically depleted in Ti (except 289) because of the poverty of their host rocks in this element as well as the frequency of

ilmenite or rutile. Hietanen (1974) found that in the contact aureole in the northern Sierra Nevada the TiO_2 content of the amphiboles depends on their rock chemistry, while Zakrutkin and Grigorenko (1967) did not find a linear relationship between the TiO_2 contents of the amphiboles and their host rocks. Like Al, Ti also depends to some extent on the bulk mineralogy. Davidson (1971) found that in ilmenite-free Quairading granulites with similar TiO_2 , the Ti content of the hornblende increases as modal hornblende decreases because little TiO_2 goes into the associated pyroxenes. The proportions of rutile, ilmenite, and biotite are also expected to influence the Ti content of these amphiboles. A broad negative relation between Al^{vi} and Ti, and $\text{Al}^{\text{vi}} + \text{Fe}^{3+}$ and Ti (Fig. 10A and B) suggests also that the entry of Ti in amphiboles is regulated by the amounts of Al and Fe^{3+} in the octahedral sites (or *vice versa*).

However, a number of workers (Engel and Engel, 1962; Binns, 1965b; De Albuquerque, 1974; Smulikowski, 1974; Ekran, 1977; Dekker, 1978) have

noted an increase in the Ti content of amphiboles with metamorphic grade; see also the experimental work of Helz (1973). The studies of Kostyuk and Sobolev (1969), Zakrutkin and Grigorenko (1966), and Raase (1974) have shown that amphiboles formed under the amphibolite facies conditions have lower TiO_2 than those of the granulite facies. Onuki and Tagiri (1972) considered that under epidote-amphibolite facies conditions the maximum TiO_2 content of the amphiboles is probably about 1%. It is interesting that only four of the Swat-Kohistan amphibolite amphiboles contain more than 1.05% TiO_2 and two of these are from a hornblende pegmatite. While it seems that an increase in metamorphic grade causes the accommodation of more titanium in amphiboles, an assessment of the metamorphic grade based solely on the TiO_2 content of the amphiboles would be meaningful only in those cases where the parent rocks are saturated with TiO_2 (*i.e.*, ilmenite- and/or rutile-bearing). A comparison of the Ti content alone in Swat-Kohistan amphiboles does not lead to satisfactory conclusions regarding the grade of metamorphism. Although the distinct difference in the Ti content of pyroxene granulites and amphibolite amphiboles may suggest some control of temperature, the Jijal granulite amphiboles have distinctly lower Ti content due to (1) generally low TiO_2 contents of the rocks, and (2) higher amounts of ilmenite and/or rutile.

Alkali content of the amphiboles

As in most other amphiboles, Na_2O is the dominant alkali but in the amphiboles from the diorites and granulites (except 24), and from five amphibolites (12, 351b, 462, 8, and 23), K_2O is also appreciable. K_2O (wt.%) exceeds Na_2O in 528, 193, 337, 192, 647, 462, and 369; however, the Na/K molecular ratio is >1 except for 528. The amount of Na + K in the formula is less than one in all but analysis 23 where it is 1.02.

As with Al and Ti, alkalis have been considered to increase with increasing grade of metamorphism (Shido, 1958; Zakrutkin and Grigorenko, 1967; Dekker, 1978; Kostyuk and Sobolev, 1969; Hietanen, 1974; Spear, 1976; Kuniyoshi and Liou, 1976). It was pointed out earlier that the Na content of the amphiboles is not dependent on that of the host rocks provided that the latter contain appreciable Na_2O . Shido (1958) found that hornblendes in the central Abukuma plateau tend to have higher alkalis in silica-undersaturated rocks than in oversaturated

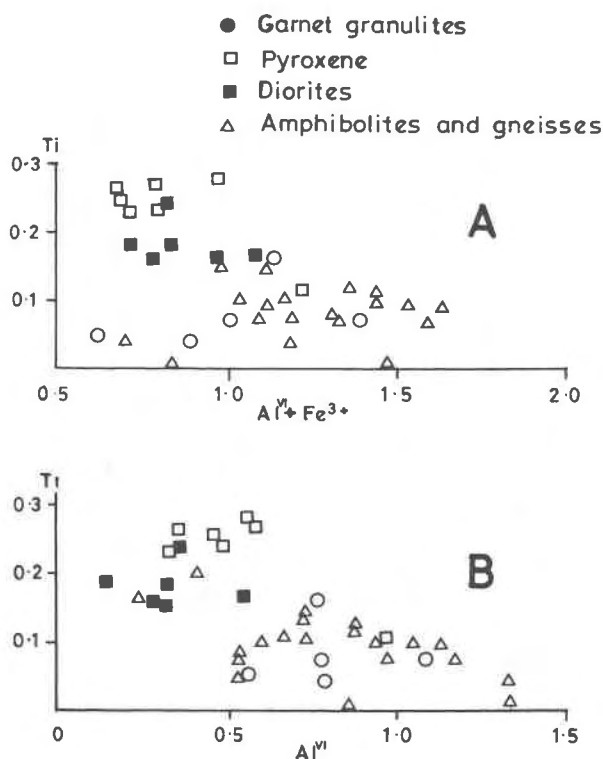


Fig. 10. Plots showing a general decrease in the Ti content with increase in $\text{Al}^{\text{vi}} + \text{Fe}^{3+}$ (A), and Al^{vi} (B). It appears that the amount of Ti in the amphiboles is regulated partly by the other charge-balancing cations in the octahedral site, including Cr in 24.

rocks but such a relationship is not found in Swat. The Na_2O contents of amphiboles from the garnet granulites is characteristically higher than those of their host rocks while in the remainder (except 24 and 23) the reverse is true. The average Na contents of the amphiboles from the various rocks are: Jijal granulites = 0.61, pyroxene granulites = 0.40, amphibolites = 0.47, and diorites = 0.33. The accommodation of higher Na in the Jijal amphiboles might be suggestive of higher pressure conditions.

The relationship between the K_2O content of the amphiboles and their host rocks is not very clear but the Jijal amphiboles are typically poor in K_2O because of the poverty of their host rocks in K_2O ; the amphiboles from diorites have quite high average K_2O because of the higher quantity of this component in their host rocks. The average K content for the amphiboles is 0.196 in the diorites, 0.269 in pyroxene granulites, 0.094 in amphibolites, and 0.022 in the garnet granulites. The average mole ratio K/Na for the amphiboles is 0.04 in the garnet granulites, 0.2 in the amphibolite, 0.7 in the pyroxene granulites, and 0.6 in the diorites. The distinct differences are interesting although we are unable to evaluate the importance of this ratio. Ekran (1977) found an increase in K with increasing grade of metamorphism in Anatolia. Rosenzweig and Watson (1954) found that hornblendes in granitized gneisses of Pennsylvania and Delaware have more K_2O and higher K/Na ratios than those from the non-granitized rocks. The Na + K in the A sites, as mentioned earlier, shows a positive correlation with temperature estimates in the four groups of rocks (Fig. 11). The granulite temperatures are average values based on up to 10 different geothermometers (Jan and Howie, 1980, 1981). The amphibolite and

diorite temperature estimates are based on Ca/(Ca+Na+K) distribution in amphibole and plagioclase (Perchuk, 1966; Spear, 1980), and for 177 and 462 also by epidote-garnet geothermometer (Dobretsov *et al.* 1972). This correlation is in conformity with the findings of Binns (1965b), Bard (1970), and Spray and Williams (1980).

By plotting Na + K vs. Ti, and Na vs. K for 182 amphiboles, Zakrutkin and Grigorenko (1967) noted that amphiboles from granulites and amphibolites plot in two distinct fields in both diagrams. Of the Swat-Kohistan amphiboles, 528, 193, 337, 24, 19, 289, 291, 462, 217 and 23 plot in the granulite field and the rest in the amphibolite field. The main reason for the plot of the latter six samples in the field of granulite amphiboles is their high Na content. The plot of five granulite amphiboles in the field of amphibolites and of three amphibolite amphiboles (19, 462, 23) in the granulite field clearly shows the inadequacy of such diagrams based on absolute concentration of elements in amphiboles. We would like to re-emphasize that bulk chemistry and mineralogy play an important role in determining the concentration of Al, Ti and, possibly, K and Na, in amphiboles and such diagrams should be used with caution.

Summary and conclusions

Calcic amphibole analyses from garnet granulites, pyroxene granulites, amphibolites, and quartz diorites of Swat-Kohistan (considered to have equilibrated at 670–770°C, 12–14 kbar; 800°C, 7–8 kbar; 570–670°C, 4–6 kbar; and 540–650°C (?), respectively) plot between tschermakite, pargasite and hornblende end-members on appropriate diagrams. They are generally rich in alumina, the most

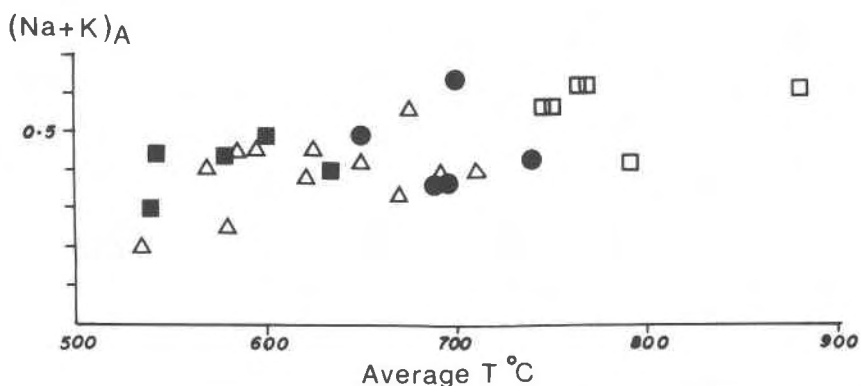


Fig. 11. Plot of $(\text{Na}+\text{K})_A$ in the amphiboles against temperature estimates for the Swat-Kohistan rocks. The diagram demonstrates an increase in $(\text{Na}+\text{K})_A$ with increasing temperature. Open squares: pyroxene granulites; solid squares: quartz diorites; open triangles: amphibolites; filled circles: Jijal garnet granulites.

aluminous being those from the amphibolite facies rocks; some of them have near maximum predicted amounts of Al^{VI} for their Al^{IV} . The amphiboles are conspicuously poor in F content.

Comparisons of the amphibole and rock analyses suggest that the Mg/Fe ratio in the hornblendes is strongly dependent, Fe^{3+} and K partly dependent, and Ca and Na independent of bulk chemistry. The quantities of Al, Ti and Na in the amphiboles are governed by bulk mineralogy which in turn is controlled by bulk chemistry and *PT* conditions including P_{H_2O} . Other factors such as f_{O_2} and the availability of charge balancing cations also variably influence the Al^{VI} and Ti contents in the amphiboles. Thus the absolute concentrations of these components (and K) cannot be used exclusively to differentiate rocks of different metamorphic grades, although Ti is highest in the pyroxene granulites amphiboles. It is probable that if P_{H_2O} is high and temperature not too high, much epidote will form, sometimes to the exclusion of plagioclase. Similarly at high *P* and *T*, abundant garnet and clinopyroxene would be expected (as in Jijal). In both cases the sodium of the rock is likely to enter amphibole and plagioclase. This probably is the reason for the substantially higher Na content of the Jijal amphiboles as compared to that of their host rocks.

The average values for (A) site occupancy and Mn contents show positive and negative correlations, respectively, with the temperature estimates for the four rock-types but other factors might also be responsible for the concentration of these components. The (OH+F) values show negative correlation with $(Na+K)_A$ and support the idea that the substantially higher than (OH,F)₂ content of some amphiboles balances the charge deficiency due to $Al^{IV} \rightleftharpoons Si$ substitution without the necessity of additional substitution of Ti, Fe^{3+} , Al^{VI} and A site occupancy.

Correlation of physical properties of the amphiboles with composition reveals that refractive indices, birefringence, and density increase and $2V(\text{calc.})$ decreases more systematically with decrease in the ratio $(Mg+Al^{VI})/(Mg+Al^{VI}+Fe^{3+}+Fe^{2+}+Ti+Mn)$. Pleochroic colors and the depth of absorption depend upon Ti, Fe^{3+} , Fe^{2+}/Mg and Fe^{3+}/Ti ratios while the angle *Z:c* increases with increase in $Fe^{3+} + Ca$.

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Appendix I. Description of hornblendes and their host rocks²

SI 283

Magnesio–hornblende with traces of Epi and Rut impurities. Absorption weak, α colorless, β faint greenish brown, γ faint brownish green. From a garnet granulite composed of Gar ($\text{Alm}_{27}\text{Gro}_{24}\text{Py}_{45}$), Hbl, Cpx ($\text{Mg}_{44}\text{Fe}_5$), with small amounts of Plg, Rut, (?)Qz. in Duber Stream, 1 km N of Ziarat, Indus Valley.

SI 297b

Magnesio–hornblende with traces of Epi and Chl. Absorption weak, α colorless, β light brown, γ light greenish brown. From a garnet granulite containing Gar ($\text{Alm}_{34}\text{Gro}_{16}\text{Py}_{46}$), Cpx ($\text{Mg}_{43}\text{Fe}_7$), Hbl, with minor Ore and Rut. 1 km E of Jijal along Indus.

SI 104b

Tschermakitic hornblende. From a garnet websterite granulite containing Opx (En_{74}), Cpx ($\text{Mg}_{41}\text{Fe}_8$), Gar ($\text{Alm}_{39}\text{Gro}_{23}\text{Py}_{37}$) and Hbl. Near contact with alpine ultramafic mass, 400 m N of Galoze Banda, along Karakoram Highway (KKH).

SI 289

Pargasite with traces of Epi and Rut. Absorption moderately strong, α yellow, β brownish green, γ brownish green. From a garnet granulite composed of 91% Par, 5% Gar ($\text{Alm}_{40}\text{Gro}_{28}\text{Py}_{28}$) and minor Ore, Rut, Cpx, Qz and secondary Epi, Chl and Sph. Along KKH, 2 km N of Galoze Banda.

SI 291

Alumino tschermakitic hornblende with 1½% Epi + Gar + Plg + Ore + Rut. Absorption weak, α yellow, β brownish green, γ bluish green. From a garnet granulite containing Gar ($\text{Alm}_{43}\text{Gro}_{21}\text{Py}_{31}$), Hbl, Plg, (An_{24}), Epi (Ps_{15}), Qz, Par (Par_{96}), Rut, Ore. 1 km N of Galoze Banda, KKH.

US 24

Titanian pargasitic hornblende with traces of Opx and Cpx. Absorption moderate, α yellow, β brown. From a websteritic pyroxene granulite containing 62% Cpx ($\text{Mg}_{43}\text{Fe}_{10}$), 19% Opx (En_{75}), 14% Hbl and 5% of secondary talc, amphibole and Ore. 4 km NE of Parao bridge, Upper Swat.

SI 192

Titanian tschermakitic hornblende with 0.4% Cpx, 0.2% Opx, 0.2% Plg and traces of ore impurities. Absorption strong, α pale

²Abbreviations: Amph amphibole, Ap apatite, Bio biotite, Chl chlorite, Cpx clinopyroxene, Ct calcite, Epi epidote, Gar garnet, Hbl hornblende, Ilm ilmenite, K–fels K–feldspar, Mus muscovite, Ore opaque minerals, Opx orthopyroxene, Par paragonite, Plg plagioclase, Qz quartz, Rut rutile, Sph sphene.

yellow, β greenish brown, γ brownish green. From a pyroxene granulite containing 76% Plg (An₅₅), 14% Opx (En₆₃), 7% Cpx (Mg₃₉Fe₁₆), 1% Hbl and minor Qz, Bio, Ore, Ap. 1 km E of Harban Stream along KKH, Indus Kohistan.

SK 528

Titanian ferroan pargasite. Moderate absorption, α pale yellow, γ olive. From a pyroxene granulite composed of 64% Plg (An₅₀), 19% Opx (En₆₀), 9.6% Cpx (Mg₃₈Fe₁₈), 5% Qz, and minor Ore, Par, Ap, Bio. In Bishigram (Madyan) stream, ½ km E of Karamai, Swat-Kohistan.

SI 217

Titanian ferroan pargasite. Absorption strong α yellow, β dark brown, γ brownish green. From a pyroxene granulite containing about 62% Plg (An₅₅), 21% Par, 8% Cpx (augite-salite), 7% Opx (hypersthene) and minor Gar, Ore, Ap, (?) Qz. 3.5 km N of Seo, along the western bank of River Indus.

SI 193

Ferroan pargasitic hornblende. Moderately strong absorption, α yellow, γ brownish green (olive). From a pyroxene granulite composed of 70% Plg (An₄₈), 7% Opx (En₅₄), 8% Cpx (Mg₃₆Fe₁₉), 10% Qz and minor Ore, Bio, Ap. Along KKH, 2 km W of Thor Stream.

SI 221

Tschermakitic hornblende containing 0.6% Qz and traces of Bio. and Plg. Absorption strong, α pale brownish yellow, β olive, γ olive green. From a pyroxene granulite composed of labradorite, Hbl, Opx (En₅₁) Cpx (Mg₃₇Fe₂₄), Qz, Ore, Bio and Ap. The hornblende replaces pyroxene and may have grown during last phases of granulite facies or top of amphibolite facies conditions. 4 km N of Richa, along Kandia River, Indus Valley.

SI 337

Ferroan pargasite. Absorption moderately strong, α yellow, β brown, γ greenish brown. From a pyroxene granulite lens in amphibolite and containing Plg (An₅₇), Opx (En₅₃), Cpx (Mg₃₇Fe₂₀), Par, Qx and minor Bio, Ore, Ap. In N of Patan fault, 1 km N of Patan, Indus Valley.

SK 647

Tschermakitic hornblende with traces of Bio and Plg. Absorption strong, α yellow, β greenish brown, γ olive. From a diorite (or retrograde granulite) containing 70% Plg (An₄₆), 13% Hbl (showing disequilibrium replacement of pyroxene), 7% Opx (En₆₁), 1% Cpx (augitic salite), 5% Qz, 2% Bio and minor Ore and Ap. Along foot path in ridge, 2.8 km W of Dabna, Swat-Kohistan.

SK 705

Magnesian hornblende with altered Bio, Epi, Qz (total 1%). Absorption moderate, α yellow, β green with brown touch, γ green. From a quartz diorite composed of 55% Plg, 12% Hbl, 20% Qz, 12% Bio and minor Ore, Ap. 6 km SW of Kalam, Swat-Kohistan. (a) Magnesian hornblende from a hypersthene-hornblende-biotite-quartz diorite, 9¼ km S. of Kalam, Swat-Kohistan. (From Jan and Kempe, 1973. Anal. C. J. Elliott, V. K. Din and A. J. Easton). Name assigned on 23 (O) basis.

SK 713

Magnesian hornblende with 2% chlorite impurity. Absorption moderately strong, α yellow, β brownish green, γ green. From a quartz diorite containing 55% Plg (An₃₅), 15% Qz, 17% Hbl, 12% Bio and minor K-fels, Ore, Ap. 6 km SW of Kalam, Swat-Kohistan.

SK 525

Tschermakitic hornblende with 1% Epi + Chl. impurity. Absorption strong, α yellow, β greenish with olive touch, γ green. From a quartz diorite composed of 57% Plg (An₄₇), 19% Qz, 6% Hbl, 15% Bio, and minor Ore, Ap. Along stream 4 km W of Kedam, Swat-Kohistan.

SK 639

Tschermakitic hornblende with 1% Epi and traces of Qz and Plg. Absorption strong, α pale yellow, β olive green, γ green. From a quartz diorite containing 52% Plg (An₃₄), 18% Qz, 18% Hbl, 7% Bio, and minor K-fels, Ore, Ap. Along Swat river in S of Peshmal, Swat-Kohistan.

Q 1

Magnesian hornblende. Absorption weak $\alpha = \beta$ colorless, γ light green. From a crudely banded rock composed almost entirely of almost equal amounts of iron-poor zoisite and grass-green amphibole with traces of Ore, Rut and secondary carbonate. Near Kotgram, about 10 km N of Chakdara, Dir. (b) Alumino-tschermakite from a corundum amphibolite, 2 km SE of Timurgara, Dir. (From Kemp and Leake, 1975).

US 12

Magnesian hornblende with 1% cloudy Epi and traces of Ilm. Absorption weak to moderate, α light yellow, β olive green, γ greenish. From an amphibolite composed of Hbl, altered Plg, Epi (Ps₂₇) and minor Ore, Cpx, Qz, Sph. In road near Chuprial, NW of Matta, Upper Swat.

SI 355

Magnesian hornblende with traces of Epi, Plg, Ore. Absorption weak, α colorless with pale yellow touch, β light yellow green, γ light olive green. From an amphibolite containing Hbl, Epi (Ps₁₀), Plg (An₆₄), and minor Sph, Qz and Ore. Along KKH, 2.5 km N of Kiru, Kohistan.

SI 352

Alumino-tschermakite. Absorption weak, α colorless, β faint green, γ light bluish green. From amphibolite consisting of amph, white mica, and minor Plg, Bio, Ore. Along KKH, ½ km N of Kiru, Kohistan.

US 19

Pargasite with traces of Chl and Rut. Absorption moderately strong, α yellowish, β green, γ greenish brown (olive). From a large pegmatite consisting essentially of Par with minor Chl, Epi, Ore, Rut. Exposed along road, 3 km S of Matta, Upper Swat.

SI 347

Tschermakitic hornblende with traces of Epi and Rut. Absorption moderate, α pale yellow, β green, γ pale bluish green. From an amphibolite containing 93% Hbl, and minor Plg (?An₄₀), Chl, Epi, Rut, Sph, Qz, Ap, Ore. Along KKH, 3.5 km NE of Kayal, Kohistan. (c) Magnesian hornblende from a hornblende pegmatite, 9½ km N of Madyan, Swat-Kohistan. (from Jan and Kempe, 1973. Anal. C. J. Elliott, V. K. Din and A. J. Easton).

SI 352b

Magnesian hornblende with traces of Sph, Qz, Plg. Absorption weakly moderate, α yellow, β green, γ pale bluish green. From a banded gneiss composed of Plg (An₃₈), Qz, Hbl, Epi, and minor Bio, Sph, Ore. Along KKH, ½ km N of Kiru, Kohistan.

US 19A

Alumino-tschermakite with 0.7% Rut + Ilm. Absorption moderately strong, α yellow, β brownish blue green, γ bluish green.

From local pegmatitic "patches" (containing Al-tsch and Epi (Ps₁₅), with minor Chl, Ilm, pyrite, Rut) in pegmatite US 19.

US 4

Magnesian-hornblende with ~.5% of Epi. + Sph. Absorption moderately strong, α yellow, β brownish green, γ bluish green. From an amphibolite containing 59% Hbl, 26% Plg (An₃₈), 7% Qz, 5% Epi (Ps₂₂), 2% Sph, and minor Ap, Ore. Exposure near main road, 6.5 km N of Khwaza Khela, Upper Swat. (d) Tschermakitic hornblende from a plagioclase amphibolite, 11½ km N of Khwaza Khela. (From Jan and Kempe, 1973. Anal. C. J. Elliott, V. K. Din and A. J. Easton). Name assigned on 23 (O) basis.

SK 462

Magnesian hastingsitic hornblende with 0.8% Epi. Absorption strong, α yellow, β olive green, γ green with bluish touch. From an amphibolite containing 43% Hbl, 34% Plg (An₅₄), 8% Epi, 7% salite, 5% Bio and minor Ct, Ap, Sph, Qz, Mus. From the isolated outcrop between road and river at Asrit, Swat-Kohistan.

US 8

Tschermakitic hornblende with traces of Epi. Absorption moderately strong, α yellow, β olive, γ bluish green. From an amphibolite composed of 58% Plg (An₄₁), 41% Hbl and minor Ap, Rut, Ore, Bio, Epi, Qz, Sph. In road-cut ½ km N of Fatehpur, Upper Swat.

SI 194

Tschermakitic hornblende with 0.5% Qz and 0.4% Rut + Ilm + Plg. Absorption moderate, α yellow, β olive green, γ bluish green. From an amphibolite containing Plg (An₄₅), Hbl, Bio, Qz,

and minor Ore, Epi, Rut, Ap. Along KKH, 20 km from Chilas towards Gilgit.

SI 177

Alumino-tschermakite. Moderately strong absorption, α pale yellow, β olive green, γ bluish green. From an amphibolite containing 64% Al-tsch, 27% Plg (An₆₂), 3% Epi (Ps₁₇), 3% Ore, 2% Gar (Alm₅₉Gro₁₆Py₂₁), 1% Ap and minor Qz. Along KKH, 1.7 km N of Jalkot, Indus Kohistan.

SI 369

Alumino-tschermakite with 1% Chl + Qz + Plg + Ore + Rut + Epi. Absorption moderate, α yellow, β olive green, γ bluish green. From a gneiss containing Plg (An₄₂), Qz, Al-tsc, Gar (Alm₅₉Gro₁₂Py₂₄), Epi (Ps₁₇) and minor Rut, Chl, Ap, Ore. In stream, 3.5 km NW of Kayal-Indus confluence, Kohistan.

SI 343

Tschermakite with 0.4% Qz, and 0.2% each of Ilm, Rut, Plg, Epi. Absorption strong, α yellow, β dark olive green, γ bluish green. From an amphibolite containing Plg (An₅₀), Tsc, Qz, Ore, Rut, Epi, Bio, Sph. Along KKH, 1 km S of Kayal, Kohistan.

US 23

Ferroan pargasite with 0.5% Qz + Rut + Epi. Absorption moderately strong. From an amphibolite containing Plg, Epi, Qz, and minor Bio, Ore, Ct, Mus, Rut, Ap, Sph. Along main road, 3.5 km E of Kabal, Upper Swat.

SI 202

Ferro-tschermakite with 0.5% Epi, 0.1% Ilm and traces of Qz. Absorption strong, α yellow, β olive green, γ dark bluish green. From a banded amphibolite containing Plg (An₄₃), Fe-Tsc, Qz and minor Ore, Bio, Epi, Sph, Rut, Ap. Along KKH 1 km S of Kayal, Kohistan.