*Geol. Bull. Univ. Peshawar, Vol. 27, pp. 1–8, 1994*

# Chemistry of hornblendes from the Deosai volcanics, Baltistan, northern Pakistan

SYED HAMIDULLAH

NCE in Geology, University of Peshawar, Pakistan

ABSTRACT: *Seventy eight core to margin spot analyses of 8 hornblende phenocrysts from an andesitic basalt of Deosai plateau, Baltistan, N. Pakistan, are presented in the form of means and standard deviations. The data show an igneous parentage for these hornblendes. Chemical variations do not agree with commonly accepted substitutions for igneous hornblendes and an overall core to margin substitution of* $[xFe^{3+}+x^{iv}Al+xTi+xMg+xNa_B = x^{vi}Al+xFe^{2+}(\pm xMn)+xCa+xSi+xA\text{-}site]$ *type is suggested with the former set of cations higher in cores and the latter in margins. A tentative temperature range of 875-700°C and a* $P_{H2O}$ *range of 6-4.2kb are suggested for the crystallization of these hornblendes. It is also suggested that like clinopyroxene the Deosai hornblendes carry unusual chemical features which may be related to variations in physio-chemical environment of the magmatic chamber, and for that reason, possibly, of the source region.*

## INTRODUCTION

The Dras volcanics of the Laddakh island arc in India overlie the Laddakh batholith and are covered by quaternary glaciofluvial and alluvial deposits. Sediments of Cretaceous age (Orbitolina limestone) are found associated with these volcanics (Desio, 1978). Detailed studies of these volcanics have been carried out in India and their compositions reported to be varying from tholeiites through andesites to shoshonites. The presence of spilites and pillow lavas has also been noticed (Riverman & Misra, 1974; Shah et al., 1976; Gupta et al., 1983; Honnegar et al., 1982; Sharma, 1991). The westerly extension of these volcanics in Pakistan are known as the Deosai volcanics. Lydekker (1883), Wadia (1937) and Desio (1978) published brief accounts of the Deosai volcanics, mainly based on field studies. Recently Hamidullah et al. (1992) described the petrography of these volcanics from Kalapani, Burzil pass, Gultari, Choota Deosai and Bara Deosai (Fig.1). Hamidullah (1991) also published a detailed description of the chemical characteristics of the clinopyroxene phenocrysts from the andesitic basalt (DW58 & DW63) of Bara Deosai, (upper reaches of Satpora River; Fig.1). This paper is an extension of the previous work (Hamidullah, 1991; Hamidullah et al., 1992), representing the interpretation of the chemistry of hornblende phenocryst from the same andesitic basalt (DW58; DW63) of Bara Deosai.

## PETROGRAPHY OF PORPHYRITIC ANDESITIC BASALT

On the basis of the various types of phenocrysts three varieties of the porphyritic andesitic basalt have been distinguished, (a)pyroxene - hornblende, (b) pyroxene-plagioclase and (c) plagioclase-phyric (Hamidullah et al.,1992). In the clinopyroxene-hornblende andesitic basalt of Bara Deosai, clinopyroxene and hornblende phenocrysts (anhedral and subhedral), up to

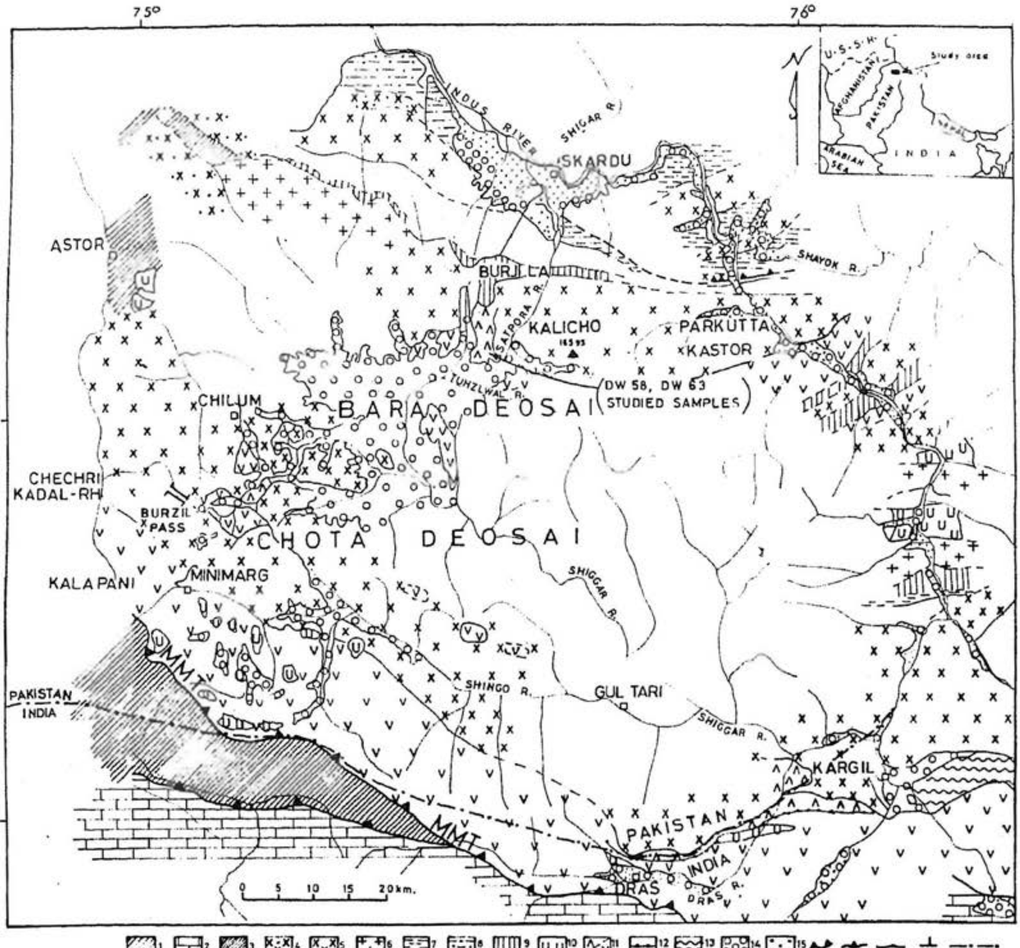


Fig. 1. Geological map of the Deosai plateau and surrounding areas, Baltistan, N. Pakistan (Modified after Desio, 1978). Outcrop boundaries of the volcanic rocks are roughly presented and are not to the scale. Legend: 1. Salkhala Formation, 2. Upper Triassic limestone, 3. Burji Formation, 4. Diorite, 5. Deosai quartz diorite & granodiorite with epidiorite inclusions, 6. Granite, 7. Gneiss, 8. Katzarah schists, 9. Hornfels, 10. Mafic & ultramafic rocks, 11. Dras volcanics, 12. "Conulites" (?) limestone, 13. Wakka Formation, 14. Glacial & fluvio-glacial deposits, 15. Alluvial deposits, 16. Overthrust, 17. Fault, 18. Limit of the formations, 19. Dip of beds, 20. International boundary.

0.5 mm in length and making a third of the total volume, lie in a fine grained matrix of plagioclase, hornblende, biotite and opaque ore. Both clinopyroxene and hornblende phenocrysts display reaction rims and are locally corroded on margins. Rarely, certain hornblende phenocrysts contain clinopyroxene cores while clinopyroxene phenocrysts contain magnetite inclusions. Some pyroxene grains are completely altered to serpentine/talc + magnetite. In pyroxene-plagioclase and- plagioclase andesitic basalts some plagioclase phenocrysts are sericitized.

## CHEMISTRY OF HORNBLENDE PHENOCRYSTS

Eight hornblende phenocrysts were analyzed from cores to margins at more then 100 spots using the Wavelength Dispersive System of the Geol. Microprobe 733, at the National Centre of Excellence in Geology, University of Peshawar. Earlier, using 23 oxygens and 13 cations (minimum $Fe^{3+}$) based formulae calculation technique (Robinson et al., 1982), all these analyses were classified as calcic hornblendes of pargasitic composition (Hamidullah et al., 1992). However, following the suggestions of Droop (1987) and Schumacher (1991) formulae were re-calculated using both the 13 (minimum $Fe^{3+}$) and 15 (maximum $Fe^{3+}$) cations methods of Robinson et al.(1982) and the means of the two sets of calculations were taken as the best estimates. Analyses with <95% totals were discarded leaving behind 78 "close to perfect" analyses. Means and standard deviations of individual phenocrysts (HBA, B, C, D, F, G, H, J) are shown in Table 1. With the exception of only three data points showing a little deviations from the main trend, the rest of the data (75 analyses) show a perfect charge balance (Fig.2a). Recalculation on 13 and 15 cation bases has raised the ferric iron of these analyses and except 4 data points indicating to be pargasites, the rest of the data exclusively fall in the field shown for magnesio-hastingsite (Fig. 2b,c).

All the data indicate igneous parentage on the $^{vi}Al$ vs $^{iv}Al$ plot of Fleet and Barnett (1978) and Ca+Na+K vs Si plot of Leake (1971) (Fig. 3a,b).

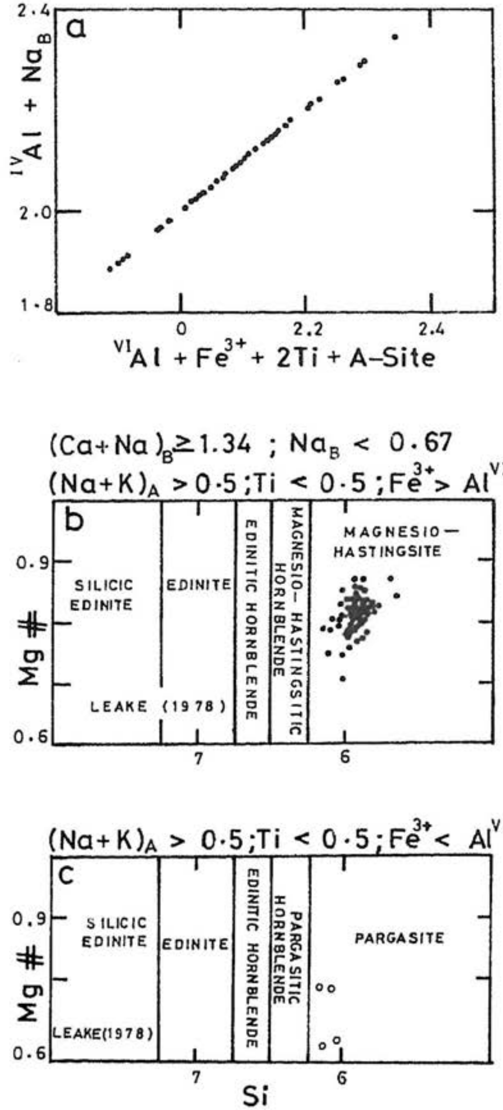


Fig. 2 (a) Charge balance and (b,c) classification plots of hornblendes from the Deosai volcanics.

### Substitutions

A tschermakitic substitution (Mg+Si = $^{iv}Al$ +$^{vi}Al$) needs positive correlation between $^{iv}Al$ and $^{vi}Al$ and between Mg and Si. Similarly an edinitic substitution (□+Si = $Na_A$+$^{iv}Al$) requires a positive correlation between $Na_A$ and $^{iv}Al$ (Helz, 1982). All such correlations are apparently absent in these hornblendes. Positive correlations of $Na_A$ with $K_A$ and $Ca_B$ are noticed (Figs. 4a,b). Such correlations negate the role of a richtiritic substitution (□+Ca = $Na_A$+$Na_B$) (see Helz, 1982).

Considering observed correlations of various cations with each other in these horn-

TABLE 1. MEANS AND STANDARD DEVIATIONS OF INDIVIDUAL HORNBLENDE PHENOCRYSTS FROM THE ANDESITIC BASALTS OF BARA DEOSAI.

| | HBA (7) | | HBB (8) | | HBC (12) | | HBD (15) | | HBF (2) | | HBG (14) | | HBH (15) | | HBJ (5) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mean | Std | Mean | Std | Mean | Std | Mean | Std | Mean | Std | Mean | Std | Mean | Std | Mean | Std |
| $SiO_2$ | 41.40 | 00.61 | 41.14 | 00.37 | 40.65 | 00.78 | 40.76 | 00.35 | 41.43 | 00.20 | 40.72 | 00.70 | 40.82 | 00.41 | 40.46 | 00.39 |
| $TiO_2$ | 01.57 | 00.19 | 01.55 | 00.16 | 02.27 | 00.27 | 02.06 | 00.13 | 02.01 | 00.14 | 02.26 | 00.12 | 01.99 | 00.19 | 02.20 | 00.18 |
| $Al_2O_3$ | 12.98 | 00.57 | 13.24 | 00.21 | 13.37 | 00.60 | 13.60 | 00.23 | 13.17 | 00.80 | 13.15 | 00.36 | 13.14 | 00.58 | 13.25 | 00.25 |
| $Fe_2O_3$ | 05.84 | 00.60 | 04.89 | 01.43 | 05.43 | 01.80 | 03.87 | 00.91 | 04.67 | 00.94 | 04.84 | 01.67 | 05.76 | 00.94 | 05.85 | 01.18 |
| FeO | 07.46 | 00.79 | 07.10 | 00.80 | 08.02 | 01.30 | 07.81 | 00.99 | 07.54 | 00.14 | 07.81 | 01.53 | 07.49 | 00.79 | 07.44 | 01.08 |
| MnO | 00.15 | 00.04 | 00.12 | 00.03 | 00.13 | 00.03 | 00.04 | 00.01 | 00.03 | 00.01 | 00.09 | 00.04 | 00.11 | 00.02 | 00.10 | 00.03 |
| MgO | 14.21 | 00.33 | 14.35 | 00.34 | 14.07 | 00.42 | 14.43 | 00.53 | 15.14 | 00.02 | 14.53 | 00.60 | 14.44 | 00.21 | 14.30 | 00.42 |
| CaO | 12.20 | 00.13 | 12.20 | 00.17 | 12.06 | 00.33 | 12.35 | 00.16 | 12.18 | 00.39 | 12.03 | 00.56 | 12.24 | 00.25 | 12.28 | 00.33 |
| $Na_2O$ | 02.41 | 00.15 | 02.46 | 00.15 | 02.55 | 00.15 | 02.81 | 00.08 | 02.85 | 00.06 | 02.70 | 00.13 | 02.72 | 00.15 | 02.72 | 00.15 |
| $K_2O$ | 00.21 | 00.05 | 00.21 | 00.09 | 00.25 | 00.05 | 00.33 | 00.05 | 00.35 | 00.04 | 00.30 | 00.07 | 00.24 | 00.04 | 00.22 | 00.05 |
| Total | 98.44 | 00.34 | 97.27 | 00.88 | 98.78 | 00.91 | 98.05 | 00.89 | 99.34 | 00.74 | 98.42 | 01.20 | 98.94 | 00.50 | 98.83 | 00.33 |
| Formulae on the bases of 23 oxygens and the mean of 13 and 15 cations | | | | | | | | | | | | | | | | |
| Si | 6.014 | 0.087 | 6.026 | 0.067 | 5.898 | 0.112 | 5.947 | 0.048 | 5.955 | 0.090 | 5.921 | 0.097 | 5.917 | 0.062 | 5.879 | 0.043 |
| Ti | 0.171 | 0.020 | 0.171 | 0.018 | 0.247 | 0.029 | 0.226 | 0.014 | 0.218 | 0.018 | 0.247 | 0.013 | 0.217 | 0.020 | 0.240 | 0.020 |
| $^{iv}Al$ | 1.986 | 0.087 | 1.974 | 0.067 | 2.101 | 0.110 | 2.053 | 0.048 | 2.046 | 0.090 | 2.079 | 0.097 | 2.082 | 0.062 | 2.121 | 0.043 |
| $^{vi}Al$ | 0.236 | 0.036 | 0.312 | 0.073 | 0.187 | 0.115 | 0.285 | 0.067 | 0.184 | 0.023 | 0.174 | 0.086 | 0.161 | 0.060 | 0.148 | 0.028 |
| $Fe^{3+}$ | 0.800 | 0.074 | 0.676 | 0.145 | 0.795 | 0.195 | 0.537 | 0.133 | 0.707 | 0.221 | 0.732 | 0.202 | 0.789 | 0.074 | 0.779 | 0.072 |
| $Fe^{2+}$ | 0.745 | 0.095 | 0.732 | 0.087 | 0.771 | 0.174 | 0.840 | 0.154 | 0.704 | 0.151 | 0.747 | 0.202 | 0.747 | 0.063 | 0.764 | 0.093 |
| Mn | 0.018 | 0.004 | 0.015 | 0.004 | 0.016 | 0.003 | 0.005 | 0.002 | 0.003 | 0.001 | 0.011 | 0.005 | 0.013 | 0.002 | 0.013 | 0.004 |
| Mg | 3.076 | 0.064 | 3.132 | 0.063 | 3.042 | 0.080 | 3.137 | 0.110 | 3.242 | 0.037 | 3.147 | 0.107 | 3.118 | 0.048 | 3.096 | 0.086 |
| Ca | 1.899 | 0.026 | 1.914 | 0.015 | 1.875 | 0.053 | 1.930 | 0.030 | 1.875 | 0.079 | 1.874 | 0.088 | 1.900 | 0.044 | 1.912 | 0.054 |
| Na | 0.678 | 0.041 | 0.698 | 0.039 | 0.717 | 0.045 | 0.794 | 0.022 | 0.793 | 0.025 | 0.761 | 0.037 | 0.765 | 0.042 | 0.767 | 0.042 |
| K | 0.040 | 0.009 | 0.039 | 0.017 | 0.045 | 0.009 | 0.061 | 0.009 | 0.064 | 0.008 | 0.056 | 0.014 | 0.044 | 0.008 | 0.041 | 0.010 |
| Mg# | 0.807 | 0.024 | 0.812 | 0.020 | 0.802 | 0.040 | 0.790 | 0.036 | 0.826 | 0.033 | 0.813 | 0.048 | 0.809 | 0.014 | 0.804 | 0.023 |

Numbers in parenthesis indicate the number of analyses averaged.

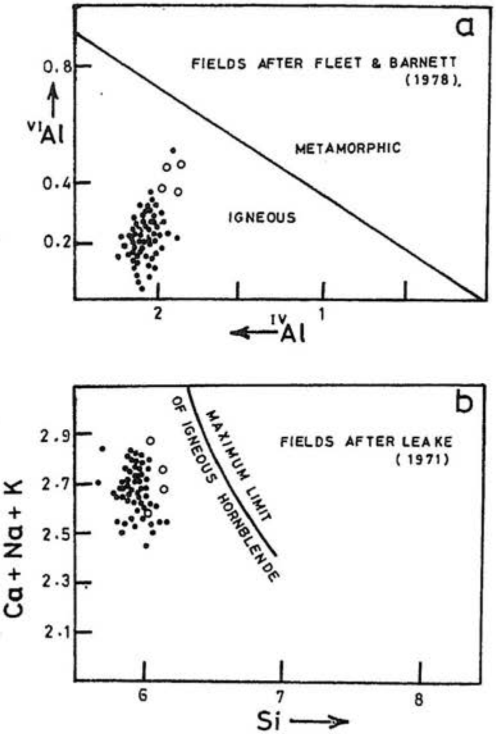


Fig. 3. (a) $^{vi}Al$ vs $^{iv}Al$ and (b) Ca+Na+K vs Si plots of hornblendes from the Deosai volcanics.

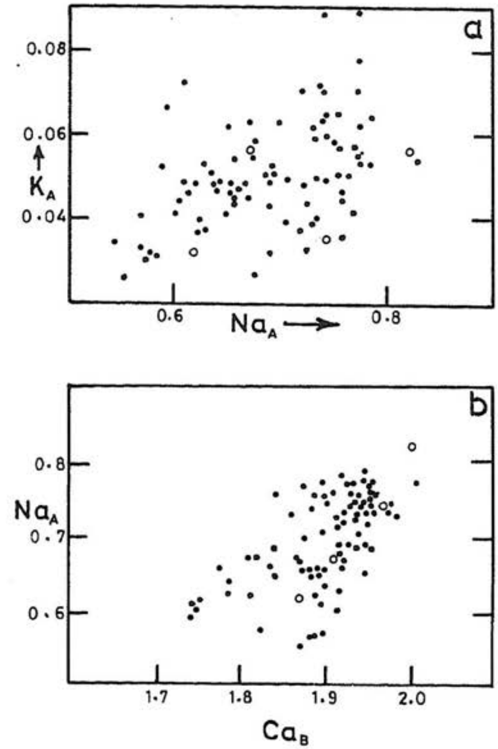


Fig. 4. (a) $K_A$ vs $Na_A$ and (b) $Na_A$ vs $Ca_B$ variations in the hornblendes of Deosai volcanics.

blende phenocrysts (not reproduced here) an overall substitution of [$xFe^{3+}$ + $x^{iv}Al$ + xTi + xMg + $xNa_B$ = $x^{vi}Al$ + $xFe^{2+}$ (± xMn) + xCa + xSi + xA-site] type is suggested with the former set of cations higher in cores and the latter in margins. ['x' is core to margin variation of individual element in each crystal or total variation of individual element in all the crystals which can be determined for each element using the method of Hamidullah (1991)]. When plotted against each other, the two sets of cations followed a negative trend with a slope value of 1.05±0.03 and R = 0.972 (Fig.5), supporting the proposed substitution.

**P-T estimates**

Experimental work has shown that hornblendes stabilizes in a temperature range of ~960-880°C and under a $P_{H2O}$ range of 18-5kb in basaltic and basaltic andesite melts (Helz 1982). No well calibrated geothermometer or geobarometer have been developed from these studies. These and other studies (Hollister et al., 1987) have however, shown that $^{t}Al$ and Ti content of calcic amphiboles are the best indicators of their pressure and temperature of crystallization, respectively. Using the technique of Hammerson and Zen (1986) and Hollister et al., (1987) revised by Johnson and Rutherford (1989) a pressure range of 6-4.2kb is determined for the Deosai hornblendes (Fig. 6a). Similarly using the Ti content of these hornblende (maximum 0.28 in crystal 'HBC' and minimum 0.14 in crystal 'HBA'), it seems that hornblendes appeared on the liquidus in a temperature range of ~875-860° and continued crystallization until the temperature dropped to ~730-695°C (Fig. 6b). It must be born in mind that these P-T

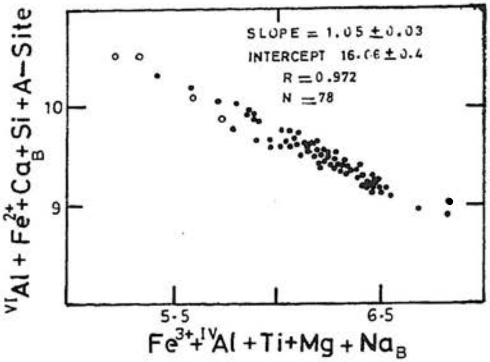


Fig. 5. Overall substitution plot of the hornblendes from the Deosai volcanics.

estimates are highly tentative as the geobarometer used was calibrated for granitic calcic hornblendes and the Ti geothermometer is based on experimental data produced under controlled buffer states which are difficult to be sorted out for the studied hornblendes., due to alterations in the groundmass (see Helz, 1982; Johnson and Rutherford, 1989). These P-T estimates however agree with the igneous parentage of these hornblendes.

## DISCUSSION

The chemistry of hornblendes from the andesitic basalt of Bara Deosai reveals that these phenocrysts are primary magmatic; an interpretation consistent with the phenocryst-groundmass relationship persisting in these rocks. The data also show that these crystals most probably crystallized in a temperature range of c.875-700°C and under a pressure ($P_{H2O} = P_{load}$) of c.6-4.2kb. Earlier, Hamidullah (1991) suggested a temperature of 1000°C and a pressure of <3kb for the clinopyroxene phenocrysts from these rocks. Petrographic observations, i.e. clinopyroxene as cores to hornblende crystals, indicate that clinopyroxene crystallized before hornblende. Therefore, both clinopyroxene and hornblende phenocrysts have grown under decreasing temperature and increasing pressure.

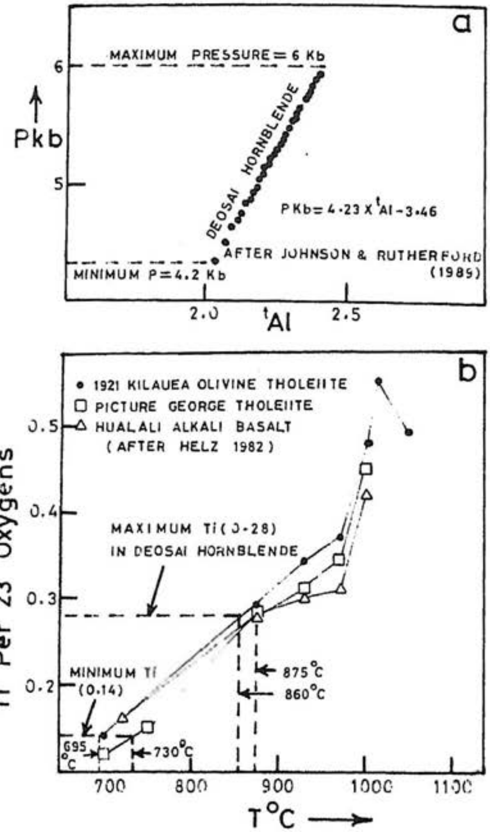


Fig. 6. (a) Pressure estimation plot for hornblendes from the Deosai volcanics.
(b) Temperature estimation plot for hornblendes from the Deosai volcanics.

On the basis of clinopyroxene chemistry Hamidullah (1991) suggested a parent magma of alkaline composition for the Deosai volcanics; with the alkalinity of magma decreasing as crystallization proceeded. This latter assumption was based on the unusual positive correlation between Ca and Na and their depletion in margins relative to cores of the clinopyroxene phenocrysts. The present study show that like clinopyroxene the Deosai hornblendes are also unusual as $Na_A$ shows a positive correlation with $Ca_B$ (Fig.4b; conversely an unusual negative correlation between $Na_A$ vs $Na_B$). As suggested earlier (Hamidullah, 1991), all such feature may probably point to changing physiochemical environment of the magmatic chamber and for that reason to changes in the source region (see Patterson & Windley, 1991). The variation from tholeiitic through calcalkaline to alkaline rocks in the Dras volcanic complex (see Gergan, 1978; Shah & Gergan, 1978) may also be related to similar processes.

## CONCLUSIONS

1. Hornblende phenocrysts in the andesitic basalt of Bara Deosai represent igneous crystallization most probably in a temperature range of c.875-700°C and under a $P_{H2O}$ of c.6-4.2kb.

2. An overall substitution of $[xFe^{3+} + x^{iv}Al + xTi + xMg + xNa_B = x^{vi}Al + xFe^{2+} (\pm xMn) + xCa + xSi + xA\text{-Site}]$ type was responsible for core to margin chemical variation in the hornblende phenocrysts.

3. Like clinopyroxene the hornblende phenocrysts from the volcanics carry unusual chemistry, probably reflecting variation in physio-chemical environments of the magma chamber and source region.

***Acknowledgments:*** Mr. Barkatullah is highly acknowledged for helping in the analyses of hornblende on electron microprobe. Ms. Malka Seem O'Zar typed the manuscript and Mr. Durrani drafted the diagrams. The NCE in Geology provided logistic support in the field.

## REFERENCES

Desio, A., 1978. On the geology of Deosai plateau (Kashmir), Mem. Sc. fisiche, ecc.- 1978 -S. VIII, vol. XV, Sez.II, p. 1-19, 4 plates.

Droop, G. T. R., 1987. A general equation for estimating $Fe^{3+}$ concentrations in ferromagnesian silicates and oxides from microprobe analyses, using stoichiometric criteria. Min. Mag., 51, 431-35.

Fleet, M. E. & Barnett, R. L., 1978. $^{iv}Al/^{vi}Al$ partitioning in calciferous amphiboles from the Frood Mine, Sudbury, Ontario. Canad. Mineral., 16, 527-532.

Gergan, J. T., 1978. Stratigraphic and tectonic studies on the Indus Suture belt between Dras and Kargil. Unpubl. Ph.D. Thesis, Jammu University.

Gupta, K. R., Gergan, J. T. & Surendar, K., 1983. Geochemistry of the volcanic rocks of the North-Western Himalayas and its bearing on tectonics- A review. In: Contemporary geoscientific Research in Himalayas volume II, (A. K. Sinha ed.). Dehra Dun, India, 9-17.

Hamidullah, S., 1991. Chemistry of clinopyroxene from the Deosai volcanics, Baltistan, N. Pakistan. Proc. 2nd Geol. Cong. Pakistan, Spec. Publ. Geol. Bull. Univ. Peshawar, 24, 161-76.

Hamidullah, S., Jan, M. Q. & Khan, B., 1992. Petrography of the Deosai volcanocs, N. Pakistan. Geol. Bull. Univ. Peshawar, 25, 17-22.

Hammerstorm, J. M., Zen, E-an., 1986. Aluminum in hornblende: An emperical igneous geobarometer. Amer. Mineral., 71, 1297-1313.

Heltz, R. T., 1982. Phase relations and compositions of amphiboles produced in studies of the melting behaviour of rocks. In: Review in Mineralogy (D. R. Veblen & P. H. Ribbe eds.), Spec. Pub. Mineral. Soc. Am. 9B, 279-346.

Hollistor, L. S., Grissom, G. C., Peters, E. K., Stowell, H. H., Sisson, V. B., 1987. Continiuation of the emperical correction of Al in hornblende with pressure of solidification of calcalkaline plutons. Amer. Mineral., 72, 231-39.

Honnegar, K., Dietrich, V. Frank, W., Gansser, A., Thoni, M. & Trommsdroff, V., 1982. Magmatism and metamorphism in Laddakh Himalayas (the Indus-Tsangpo suture zone). Earth Planet. Sci. Lett., 60, 253-92.

Johnson, M. C. & Rutherford, M. J., 1989. Experimental calibration of aluminium-in-hornblende geobarometer with application to Long Valley Caldera (California) volcanic rocks. Geology, 17, 837-841.

Leake, B. E., 1978. Nomenclature of amphiboles. Amer. Mineral., 63, 1023-1053.

Leake, B. E., 1971. On aluminous and edinitic hornblendes. Min. Mag., 38, 389-407.

Lydekker, R., 1883. The geology of the Kashmir and Chamba territories, and British district of Kaghan. Mem. Geol. Surv. India, 22, Calcutta.

Patterson, M. G., & Windley, B. F., 1991. Changing source regions of magmas and crustal growth in the Trans-Himalayas: Evidence from the Chalt volcanics and Kohistan Batholith, North Pakistan. Earth Planet. Sci. Lett., 102, 326-341.

Raiverman, V., & Mishra, V. M., 1974. Suru tectonic axis, Laddakh area. Geol. Min. Met. Soc. Ind. Golden Jubilee Symp (Abst).

Robinson, P., Spear, F. S. & Schumacher, J. C., 1982. General review of metamorphic amphibole compositions. In: Review in Mineralogy (D. R. Veblen & P. H. Ribbe, eds.), Spec. Pub. Mineral. Soc. Am., 9B, 3-9.

Schumacher, J. C., 1991. Empirical ferric iron corrections: necessity, assumptions and effects on selected geothermobarometers. Min. Mag., 55, 3-18.

Shah, S. K., Sharma, M. L., Gergan, J. T. & Tara, C. S., 1976. Stratigraphy and structure of the Western part of the Indus suture belt. Laddakh, Northwest Himalayas. Him. Geol., 6, 534-56.

Shah, S. K. & Gergan, J. T., 1978. Geochemistry of Dras volcanics and its tectonics significance. 9th. Him. Geol., Sim. Abst.

Sharma, K. K., 1991. Tectonomagmatic and sedimentation history of Laddakh collision zone: A synthesis. Physics & Chemistry of the Earth, In: Geology and Geodynamic evolution of the Himalayan collision zone, part 1 (K.K. Sharma, ed.), 17(2), 115-132.

Wadia, D. N., 1937. The Cretaceous volcanic series of Astor, Deosai, Kashmir and its intrusions. Rec. Geol. Surv. India, 51, 185-370.