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Petrochemistry of asbestos bearing rocks from Skhakot-Qila Ultrmafic Complex, northern Pakistan

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Abstract

This study has been carried out to map asbestos deposits of the Skhakot-Qila Ultramafic Complex around Peshawar valley and to describe their petrochemical characteristics. Dunite, peridotite, serpentinite, chromitite and mafic rocks are the main types of the complex while tremolite, talc-carbonate, steatite and chlorite wall rocks are found in the form of irregular to pod like, elongated or tabular masses and veins transacting the ultramafic rocks along shear zones. The serpentine in the complex is classified as chrysotile and has grown along shear zones as fibrous asbestos. Asbestiform tremolite occurs locally at Newe Killi, Hero Shah and Behram Dehri and has most probably grown from the deformation of pyroxenite.

The data indicate that rocks of the Skhakot-Qila Ultramafic Complex represent an ophiolite segment of the Thetyan ocean crust and are classified as a partly metamorphosed mafic ultramafic complex. Igneous crystallization and fractionation and accumulation of olivine, pyroxenes and chromite have led to the development of mafic and ultramafic rocks. Tectonic emplacement has caused the deformation and metamorphism of these rocks transforming dunite and perodotite into serpentine. Local variation in P-T condition during tectonic deformation and metamorphism caused the recrystallization of various minerals with serpentine as essential constituent and brucite, forsterite, magnetite, magnesite, talc and carbonate associated in various proportions.

1. Introduction

Asbestos is the fibrous form of mineral silicates belonging to the serpentine and amphibole groups of rock-forming minerals. It has been used in commerce since the beginning of the industrial era. Presently it has been used in more than 3000 products (Shirde, 1973; Jehan, 1996). Asbestos occurs in many parts of northern and northwestern Pakistan (Qaisar et al., 1967; Jehan and Khan, 1963; Qaisar and Khan, 1967). These occurrences are largely confined to the ultramafic rocks (dunite-peridotite, pyroxenite) of possible ophiolitic affinities associated with the Main Mantle Thrust (Asrarullah et al., 1979, Tahirkheli et al., 1979). Two of the major belts of such ultramafic rock occur in Malakand and Mohmand agencies and district Charsadda (Rafiq, 1984). These are described as Skhakot Qila Ultramafic Complex (SQUC) with particular reference to the genesis of chromite (Ahmed, 1982). The Mohmand agency, ultramafic complex is a western extension of the rocks in Malakand agency and district Charsadda. Hamidullah (1984) reported two new localities from Bucha, Prang Ghar area of Mohmand agency.

The present work has been carried out to map the geology of the asbestos-bearing rocks of the SQUC and to describe their petrochemical features.

2. Regional geology

The geological and tectonic features developed in the northern part of Pakistan are the product of collision of Eurasian plate with Indian plate, 55 m.y. ago (Powell, 1979). This collision occurred due to northwards subduction of Tethys ocean floor under the Eurasian plate. The Kohistan island arc formed in response to this subduction during the Cretaceous and was sandwiched between the two mighty continents, (Eurasia and Indo-Pakistan) during early Tertiary. The northern and southern limits of Kohistan island arc are marked by two branches of the Indus suture zone which marks the collision line of India and Eurasia in Tibet (Desio, 1964). The northern one, the Hini-Chalt-Yasin-Drosh fault is called Main Karakoram Thrust (MKT), (Tahirkheli et al., 1979). It separates the Kohistan arc from Eurasia. The southern one is traced along Babu Sar-Utla-Jijal-Shangla Mingora and Khar, and has been named as Main Mantle Thrust (MMT) (Tahirkheli et al., 1979) along which the Kohistan island arc is wedged with Indo-Pakistan plate (Fig.1).

The rocks of the Main Mantle Thrust in the lower Swat are known as the Indus melange group (Kazmi et al., 1984) whereas in the Malakand and Mohmand agencies and district Charsadda these have been described as an ultramafic complex of Skhakot-Qila, Harichand and Dargai (Ahmad, 1982; Rafiq, 1984). Here the sack name Skhakot Qila Ultramafic Complex (SQUC) has been used, instead. The rocks of the MMT comprise fragmented blocks derived from oceanic crust, volcanic arcs, trenches and continental margins ranging from Precambrian to Late Cretaceous in age. Figure 2 shows the distribution of ultramafic rocks in the study area in Malakand and Mohmand agencies and Charsadda district.

3. Local geological setting

The SQUC asbestos deposits are associated with a complex of dunite, harzburgite and chromitite rocks extending from Skhakot and Dargai to Mohmand Agency for a linear belt of about 40 Km with a 2-5 Km width (Fig. 2). The complex has an east-west strike with a north-west dip ranging from 60 to 90 degrees and is partly in contact with a series of low grade (metasediments). The ultramafic rock extends westward to Khyber Agency and also occurs in Logar province of Afghanistan. Outcrops of metasediments along the northern and western borders of the complex are chlorite schist and phyllite, biotite-muscovite-quartz schist and soapstone. A small elongated body of metagabbroic rock separates the ultramafic complex and schistose metasediments in west of Hero Shah (not visible on map). Another metagabbroic rock is exposed in the south of Usmankhel Garhi, i.e. south-east of Darwazgai (Fig.2).

Nearly two third of the ultramafic mass is composed of harzburgite with small conformable but randomly spreaded outcrops of dunite rock. There are three dunite-harzburgite exposures which are partly or completely surrounded by peridotite. The peridotite is in turn surrounded by a narrow zone of serpentinite with asbestos occurring along the contact of ultramafic complex with metasediments and other enclosing rocks.

Dunite is generally barren, but infrequent chromite concentrations constitute chromitite rocks. The entire ultramafic complex is sporadically traversed by thin pyroxenite dikes. At places veins of tremolite talc, tremolite, talc-carbonate and quartz rocks are abundant. (Ahmed, 1978; Rafiq, 1984; Rafiq et al., 1983; Rafiq et al., 1984; Uppal, 1972; Jehan, 1997).

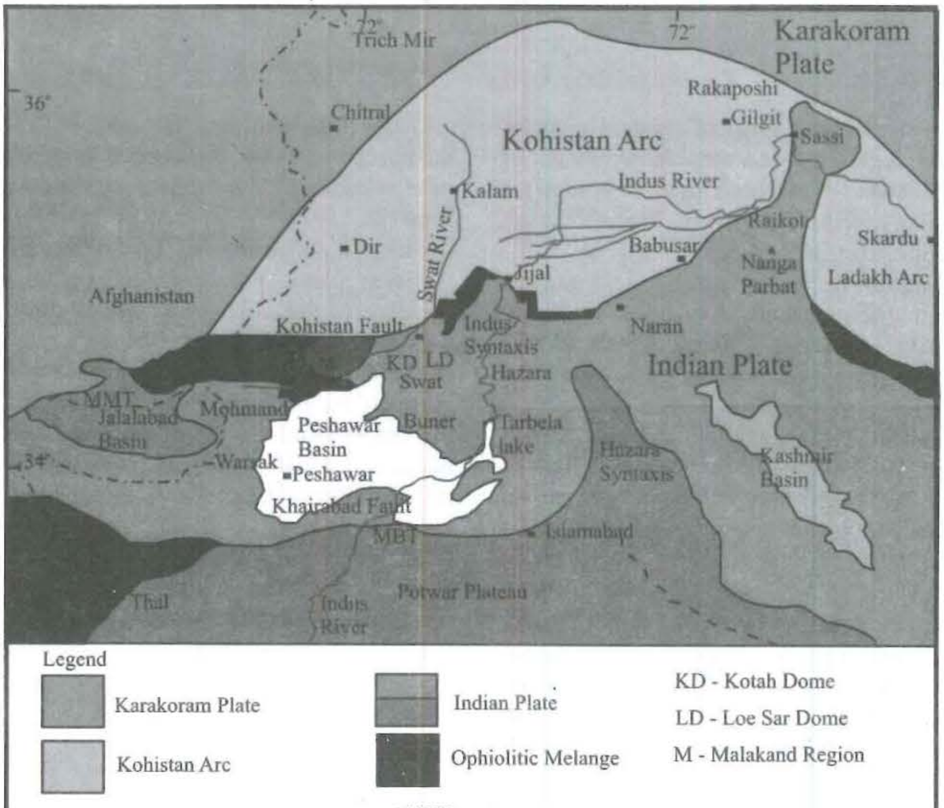

Fig. 1. Tectonic map of the Western Himalaya. The ophiolitic mélange units collectively form the Indus suture zone which is also known as the Main Mantle Thrust (MMT) in Pakistan (Modified after DiPietro and Isachen, (2001). Box shows the study area.

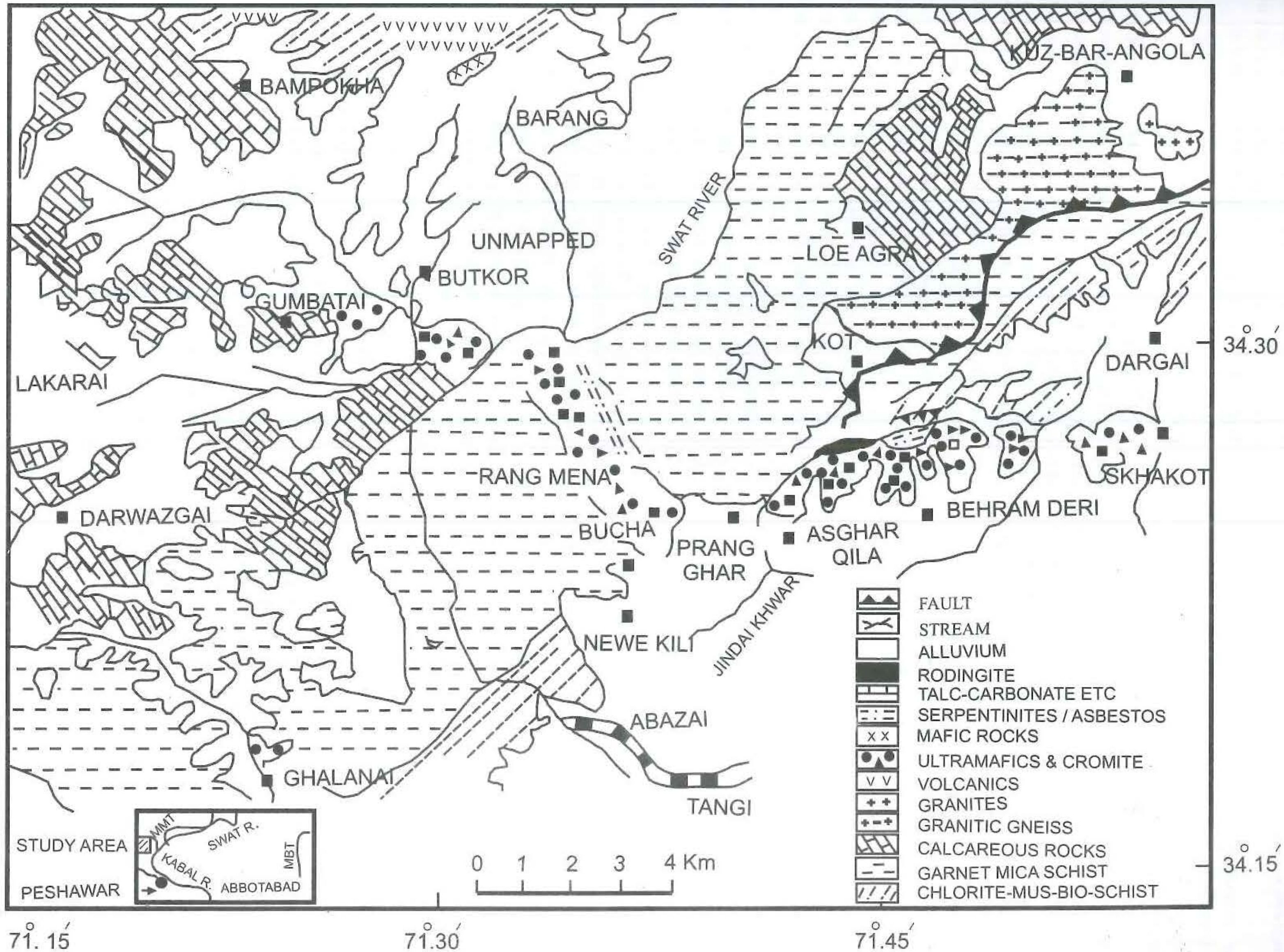

Fig. 2. Geological map of the SQUC (modified after Rafiq, 1984)

4. Petrography

The various types of rocks of the study area are briefly described here.

4.1. Ultramafic rocks

4.1.1. Dunite

Dunite interlayred with peridotite is the dominant ultramafic member of the complex (Uppal, 1972). It is a medium to coarse-grained rock which contains >90% olivine (fo_{88-92}), pyroxene 0-11% and opaque ore (mainly chromite) 0-5% as primary constituents. In relatively altered varieties 25-50% olivine has altered to serpentine and magnetite and rocks with >50% serpentine are rather classified as serpentinite than dunite. Olivine occurs in cores of chromite crystals which are again surrounded by olivine megacrysts, forming corona structure.

Olivine alteration occurs in two ways. (a) Pseudomorphs of serpentine and magnetite perfectly retaining the original grain size and shape, with magnetite concentrating along cracks. In such cases alteration seems to be mainly due to addition of water with little involvement of directed pressure, as the pseudomorphs do not show any signs of deformation. At other places, i.e., closer to the vicinities of asbestos zones deformation becomes evident both in olivine and its pseudomorphs. In such rocks alteration to fine-grained serpentine increases and crystals/pseudomorphs slowly are loosing their outlines. (b) A second phase serpentinisation is also noticed along cracks, cross cutting both olivine and olivine pseudomorphs in the same rock.

4.1.2. Serpentinite

There are two types of serpentinites. The massive serpentinite type contains relic olivine, olivine pseudomorphs, serpentine + magnetite, magnesite, chromite, brucite, chlorite and carbonate. In friable serpentinite serpentine occurs as very fine to large flakes. chromite is associated in two different forms: patterned crystals initially associated with zoned olivine along zones, from which the olivine part has been completely serpentinized to large flakes serpentine and as well small disseminated grains with relatively small flakes of serpentine.

4.1.3. Peridotite

Samples from behram dheri containing 10-30% pyroxene, mostly clinopyroxene with dominant olivine are classified as peridotite. Other constituents in these types are chromite, magnetite, carbonate, talc and accessory plagioclase. Olivine is similar to that described in dunite and has partially or totally altered to serpentine. On the basis of the presence of both clino- and ortho-pyroxenes, peridotites can be classified as wehrlite and harzburgite. Pyroxene in peridotite is kinked and banded and also shows schiller structure providing evidences of cataclasis. The kinked pyroxene show wavy extinction.

4.2. Mafic rocks

Mafic rocks include meta-gabbros and meta-basalts. The former are coarse-grained rocks exposed at Rangmena, Kawal, Kotagai, Gumbatai and Lakarai, containing plagioclase $_{(An_{65-73})}$ (50-60%), clinopyroxene (15-20%), orthopyroxene (5-8%), biotite (1-4%) and opaque ore (2%). At Behram Dheri a hornblende-gabbro occurs, which contains hornblende (50%) and plagioclase (45%) with opaque ore (5%). Hornblende is partially chloritized and plagioclase is cloudy and epidotized. Opaque ore is both chromite and magnetite. The latter seems to be a by-product of the chloritization of hornblende. Similar rocks are also exposed in Bucha area at the southern extremity of the complex containing fresh hornblende crystals with plagioclase set in relatively fine- grained matrix of plagioclase, hornblende and epidote. Considering its porphyritic appearance this rock can be classified as porphyritic microgabbro. Associated with these microgabbros are more fine-grained rocks in which plagioclase phenocrysts containing clinopyroxene core are set in a highly chloritized ferromagnesian matrix. Fresh pyroxene grains in the core of plagioclase crystal indicate that the order of primary crystallization was pyroxene - plagioclase. Rutile is also noticed in these meta-basalts. As mentioned earlier other significant rocks associated with ultramafic and mafic types are talc-carbonate rocks and carbonate quartz rocks.

4.2.1. Asbestos types

The asbestos of various localities (i.e., Behram Dheri, Hero Shah, Newe Killi, Narai Obe, and Qila) have been analyzed by X-ray diffractometer in the National Centre of Excellence in Geology, University of Peshawar. The data show that the asbestos from these localities is generally chrysotile with local occurrences of antigorite and tremolite.

5. Geochemistry

The major element analyses of the samples were performed using atomic absorption spectrophotometer in the National Centre of Excellence in Geology, University of Peshawar.

5.1. Geochemical affinity

The petrographic classification of the various rock types described above is reflected in their chemical composition. Except the two serpentinite samples, others are showing alkalis between 4-5 wt% and SiO_2 between 35-52%, all the ultramafic rock plot below the boundaries defined for basaltic rocks on the Alkali vs

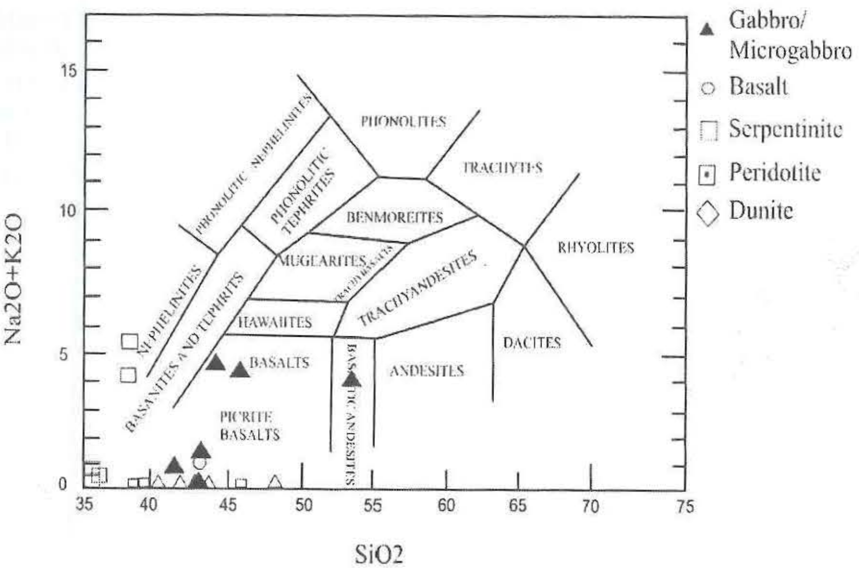

Fig. 3. Alkali vs SiO_2 classification diagram for SQUC. Fields are after Cox et al. (1979).

SiO_2 classification plot of Cox et al. (1978), indicating their cumulate nature. On the other hand the gabbros, micro-gabbro and volcanic rocks plot in the fields defined for basalt, picric basalt and one in the field of andesitic basalt (Fig. 3).

On an AFM plot dunites and peridotite plot in the ultramafic ophiolite field while the gabbros, microgabbro and basalt occur in fields of island arc cumulates and non-cumulates (Fig. 4). On the CaO-Al_2O_3-MgO plot (Fig. 5) most of the ultramafic rocks fall in the fields of ultramafic cumulates and metamorphic ultramafic cumulates. The mafic rock mostly occurs within or close to the field of mafic cumulates.

5.2. Major elements

On the MgO vs oxide plots (Fig. 6), the data though generally show scatter however, SiO_2, CaO, Al_2O_3, TiO_2, MnO and K_2O have negative correlations with MgO. A gap between the mafic and ultramafic rock exists which may be related to sampling gap or more typically to the appearance of plagioclase as one of the dominant minerals on liquidus in the former types.

This gap may also be related to partial genetic disconformities between the mafic and ultramafic rocks as would be expected from a collage of an ophiolitic melange zone. The Al_2O_3 vs MgO plot show a better correlation than the others indicating the absence of plagioclase as a dominant phase on the liquidus. The CaO vs MgO plot has a higher scatter than Al_2O_3 vs MgO, indicating the distribution of CaO both in calcic pyroxene and the residual liquid.

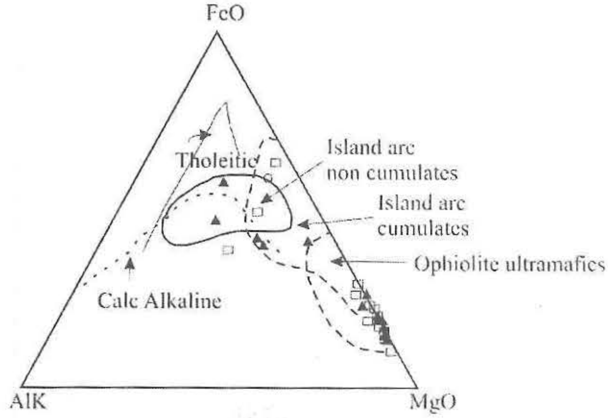

Fig. 4. AFM plot of rocks from SQUC. Fields after Irvine and Baragar (1971).

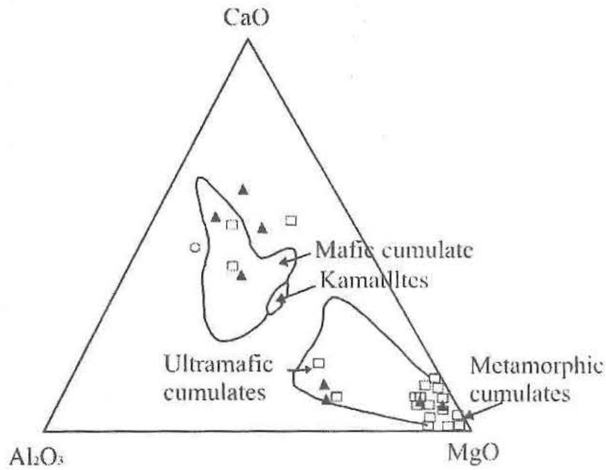

Fig. 5. Tectonic discrimination plot of the SQUC on the basis of CaO-Al_2O_3-MgO. Fields after Coleman (1983).

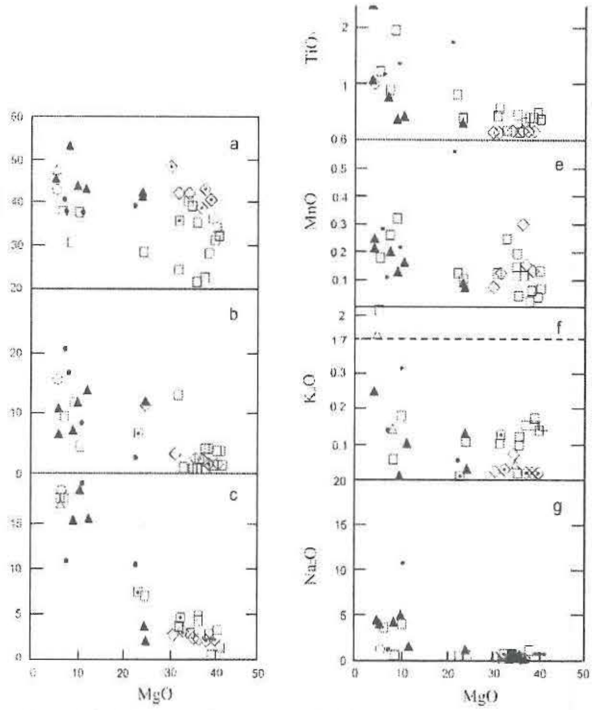

Fig. 6. SiO_2, CaO, Al_2O_3, TiO_2, MnO, K_2O and Na_2O vs MgO plots of rocks from SQUC.

The Al_2O_3 vs MgO plot is one-evidence that the two sets of rocks are most probably related to each other by partial melting and/or crystallization differentiation. The scatter in other plots reflects most probably contamination during serpentinization and other alteration processes related to tectonic events. The presence of carbonate and quatrzofeldspathic veins confirms these transformations.

5.3. CMAS plots

In a projection from En (MS) to Ol (M_2S)-Pl (CAS_2)-Di (CMS_2) most of the serpentinites, partially altered dunites and peridotite follow a linear trend perpendicular to the Ol- Pl join, close to the Ol corner and away from the triangle, indicating olivine fractionation and a systematic variation in the chemistry (Fig. 7). The micro-gabbros follow a general trend from the Pl apex towards the En position and then turning towards the dunites trend (through a couple of serpentinites) indicating a continuation in chemistry of the two sets of rocks (at least the course-grained facies). The mafic rocks indicate orthopyroxene + plagioclase fractionation as the dominant controlling phenomenon. Certain serpentinites, one partially altered dunite and one peridotite sample lies close to Pl corner. These samples may contain a large proportion of plagioclase but their extensive alteration does not let this to be confirmed petrographically. In addition these samples are also carbonated, some of them extensively, and their greater affinities towards Pl corner may be related to this phenomenon. It is worth noticing that the microgabbros and basalt samples plot close to the Pl apex indicating a high degree of plagioclase fractionation. In a projection from Di to Ol-Pl-Qtz the gap noticed between the mafic and ultramafic groups on oxide MgO plots is more visible (Fig. 8); most of the ultramafic rocks lie close to the Ol corner and the basic ones close to the Pl corner along the Ol-Pl join. Both show limited affinities towards Di.

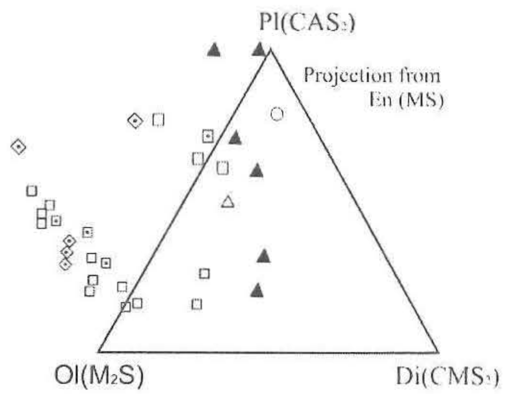

Fig. 7. Compositional variation of rocks from the SQUC shown in a projection from MS into M_2S-CAS_2-CMS_2 plane of the CMAS quadrilateral of Cawthorn & O' Hara (1976). En=Enstatite; Ol=Olivine; Di=Diooside

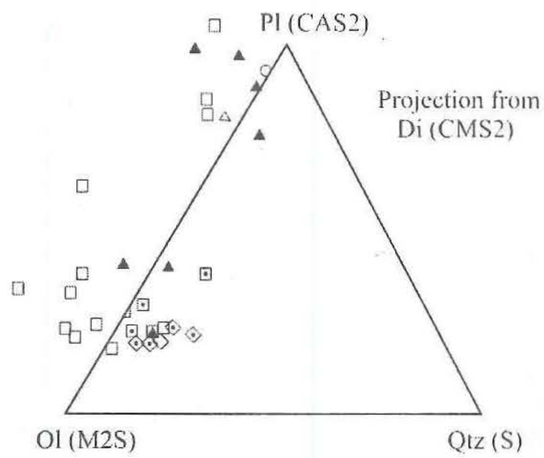

Fig. 8. Compositional variation of the rocks from the SQUC shown in a projection from CMS_2 into M_2S-CAS_2-S plane of the CMAS quadrilateral of O' Hara (1968). Di=Eiopside; Ol=Olivine; Pl=Plagioclase; Qtz=Qaurtz.

These observations indicate the data can be chemically divided into two groups, (i) ultramafic rocks with a dominant olivine fractionation and limited incorporation of opx and/or cpx, on the liquidus and (ii) the mafic rocks with dominant orthopyroxene and plagioclase fractionation. Considering petrographic characters this group can be further divided into two groups, (a) the microgabbros dominated by plagioclase

+ orthopyroxene fractionation and may be possibly termed micronorites rather than microgabbros, and (b) the micro-gabbros and basaltic member indicating the dominant plagioclase fractionation. Similar conclusions can be drawn when those data were plotted on other projection of O'Hara (1976) and in CMAS projection devised by Cawthorn and O'Hara (1976) and Grove et al. (1982; Fig. 9 and 10).

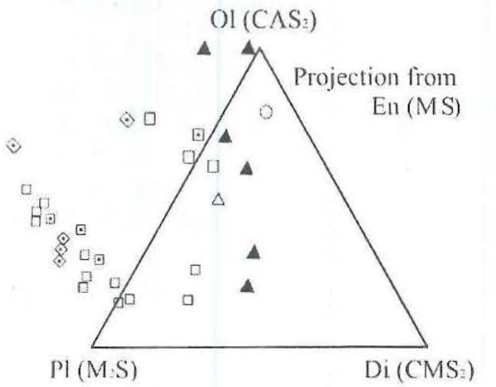

Fig. 9. Compositional variation of rocks from the SQUC shown in a projection from MS into M_2S-CAS_2-CMS_2 plane of the CMAS quadrilateral of Cawthorn & O' Hara (1976). Ol=Olivine; Pl=Plagioclase; Di=Diooside

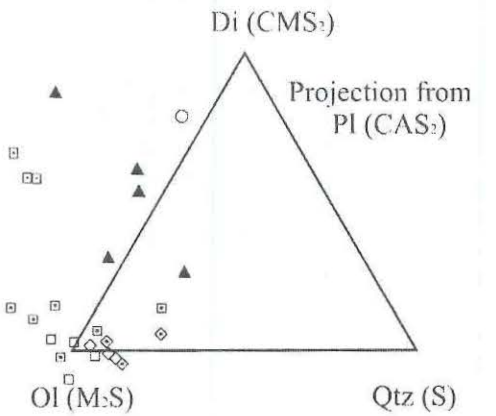

Fig. 10. Compositional variation of rocks from the SQUC shown in a projection from CAS_2 into M_2S-CMS_2-S plane of the CMAS quadrilateral of Grove et al. (1982).

6. Discussion

The Skhakot Qila Ultramafic Complex has been described as an ophiolite segment of the Tethyan oceanic crust (sandwiched between the Gondwanic continent and Kohistan arc - generally exposed along MMT), tectonically emplaced in the present location (see Ahmed and Hall, 1982a; Tahirkheli et al., 1979). Ahmed (1982) has referred it to the harzburgite sub-type of Alpine type peridotite of Jackson and Thayer (1972).

The tectonic settings, field relationship, petrographic and chemical data of the ultramafic and related rocks (gabbros, microgabbro, metavolcanic) support the previous work. The ultramafic rocks, dunite, pyroxenite and peridotite have major element character typical of metamorphosed ultramafic cumulate. Similarly the limited data on the basic rocks also indicate oceanic character. Therefore, both the sets of rock can be tectonically classified as rocks of an oceanic mafic-ultramafic complex. Major element chemistry indicates initially the role of igneous crystallization differentiation with olivine and pyroxene as dominant phases on the liquidus in ultramafic rocks. The role of plagioclase fractionation seems meager as no plagioclase-rich ultramfic rocks occur in the complex and plagioclase if present is interstitial and accessory. Petrography and chemical data indicate pyroxene and plagioclase as the dominant crystallizing phases on liquidus in the mafic rocks. This is supported by the presence of plagioclase pseudomorphs and epidote after pyroxene in these rocks.

The dominant post solidification transformation is serpentinization of dunite and peridotite, and the formation of chlorite and epidote in the mafic rocks. A variety of other secondary minerals associated with serpentine locally in dunites/serpentinite and peridotite/serpentinite are magnetite, asbestos (chrysotile, tremolite), magnesite, brucite carbonate and talc. Hamidullah (1984) working at Bucha, Mohmand Agency on the petrogenesis of asbestos referred the transformation of dunite/peridotite to serpentinite according to the reaction of Coleman and Keith (1971) and Moody (1976a, b) as following: Olivine + H_2O Serpentine + Brucite + Magnetite. He signified these transformations under high temperature and oxygen fugacity and referred the presence of talc at certain localities to the presence of CO_2. On the basis of asbestos associated typically with shear zones and the presence of slickensides and mylonite he attributed the formation of this fibrous mineral to increased directed pressure, locally during tectonic emplacements. On the other hand Jehan and Khan (1963) reported spheroidal asbestos from Qila, attributed the origin of asbestos to (a) the transformation of olivine to serpentine under hydrothermal alteration, (b) the formation of a mixture of magnesium silicate and water constituting a binary system of immiscible liquid, (c) subsequent cooling resulting into spheroids of asbestos in water, (d) further cooling resulting into massive serpentine enveloping the spheroids. As both slip fiber and spheroidal asbestos are present at Qila, Bucha and all other localities, it is suggested that both the phenomenon were operative at different places and wherever P_{co_2} increased 5 mole %, talc instead of chrysotile/asbestos formed, particularly under directed pressure (see Moody 1976a, b; Johannes, 1968). The overall petrographic and chemical data and previous studies indicate that the ultramafic rocks of SQUC have undergone the following stages of evolution:

a) Emplacement of basic magma under oceanic environment in magma chamber under the Tethyan oceanic crust.
b) Crystallization differentiation and accumulation of olivine, and/or pyroxene resulting into layered dunite, peridotite and pyroxenite as the ultramafic members of the complex.
c) Tectonic emplacement of the complex during Himalayan orogeny.
d) Metamorphic transformation due to changes in P-T regimes resulted in the formation of serpentine after olivine and pyroxene, tremolite after pyroxene, in the ultramafic rocks and chlorite and epidote after pyroxene and plagioclase in the basic rocks; indicating at least green schist facies environment (Miyashiro, 1973).
e) Other minerals which developed during metamorphism and tectonic processes are asbestos, talc, brucite, various carbonates, magnetite and magnesite. Asbestos is represented by tremolite after pyroxene and by chrysotile after olivine and orthopyroxene. As mentioned earlier other phases associated with serpentine including talc, brucite magnetite etc. all indicate local variations in P-T conditions (i.e. brucite - low temperature serpentinization, talc-low P_{CO_2}, asbestos - high P_{CO_2}, talc + magnesite intermediate fO_2 and fS_2; see Moody 1976a).

Previous studies (Jehan and Khan, 1963; Qaisar and Khan, 1967; Arif, 1994) and the current data including XRD results indicate that at Bucha, Prang Ghar, Newe Killi, Narai Obe, and Hero Shah the dominant variety of asbestos is chrysotile, associated by tremolite and antigorite.

7. Conclusions

Rocks of the Skhakot Qila Ultramafic Complex represent an ophiolite segment of the Tethyan oceanic crust and are classified as a metamorphosed mafic ultramafic complex. Igneous crystallization, fractionation and accumulation of olivine, pyroxenes (and chromite) led to the development of dunite, harzbargite pyroxenite (and chromitite) and fractionation of pyroxene and plagioclase led to the development of gabbros, microgabbros and volcanic members of the suite (Bucha). Tectonic emplacement led to deformation and metamorphism of these rocks transforming dunite and peridotite into serpentinite. Local variation in P-T condition during tectonic deformation and metamorphism caused the crystallization of various minerals with serpentine as essential constituent and brucite, forsterite, magnetite, magnesite, talc and carbonate associated in variable proportions. Serpentine is classified mostly as chrysotile and along shear zones it is grown as fibrous asbestos. Asbestiform tremolite also occurs locally at Hero Shah, Behram Dheri and Newe Kili and has most probably grown from the deformation of pyroxenite.

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