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Characteristics of ultramafic rocks and associated magnesite deposits, Nal Area, Khuzdar, Balochistan, Pakistan

Erum Bashir¹*, Shahid Naseem¹, Tabinda Akhtar² and Khula Shireen³

¹Department of Geology, University of Karachi, Karachi 75270, Pakistan. ²Petrography Laboratory, Geological Survey of Pakistan, Gulistan-e-Johar, Karachi, Pakistan. ³PCSIR Laboratories Complex, off University Road, Karachi, Pakistan.

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The Bela Ophiolite (BO) is part of the Alpine-Himalayan orogenic belt. Rocks of BO were formed in both MORB and suprasubduction zone settings and include both ultramafic and mafic compositions. The ultramafic rocks were serpentinized after harzburgite. Orthopyroxene is more abundant than clinopyroxene. Serpentine commonly occurs as angular and medium sized fragments exhibiting mesh texture and within veins. Serpentine is associated with variable percentages of chlorite, magnetite, actinolite, talc, brucite and calcite. Shearing and faulting obliterated the primary textures and resultant microfractures permeate the rocks. On an AFM diagram samples from the study area plot in the field of metamorphic peridotite and ultramafic rocks of ophiolitic affinity. On a TAS diagram, the samples reflect a tholeiitic source that was generated at very high temperature, most commonly at a MORB setting. High range of Mg# 97.5 - 82.6 and low values of differentiation index (0.7 - 7.7) suggest primitive mantle compositions. The ultramafic rocks of the study area were serpentinized and subsequently altered into hydrothermal magnesite, hydromagnesite and brucite. The magnesite and associated hydromagnesite indicate formation within a low temperature regime. On a Fe versus Mn plot, and the average Cr/Mg, Fe/Mg and Mn/Mg values revealed that the studied magnesites were genetically affiliated with cryptocrystalline Kraubath type of magnesite.

Key words: Khuzdar, magnesite, Pakistan, petrography, ultramafic rocks.

INTRODUCTION

Ultramafic rocks have received considerable attention within the geological community in recent years because they provide excellent opportunities to gain insight into the inaccessible realm of mantle rocks. Mostly they are formed by the partial melting of upper mantle and facilitate in the understanding of the details of fractionation, origin, tectonic history and other petrological processes (Raymond, 2002). Ultramafic rocks act as hosts for Cr, Ni, Cu and PGE mineralization.

Serpentine is the weathering product of ultramafic rocks and has an affiliation with a variety of fascinating mineral models. The serpentinized ultramafic rocks can host cryptocrystalline magnesite, talc-magnesite and anthophyllite asbestos deposits (Simandl and Ogden, 1999) as well as brucite deposits (Antonio and Kristensen, 2004). Serpentinite has been long known to host unusual minerals such as awaruite ($FeNi_3$), heazlewoodite (Ni_3S_2) and hydrogarnet that are rarely found in any other geological environment (Frost and Beard, 2007).

The ultramafic rocks of Nal area are the northern segment of the Bela Ophiolite (Figure 1) and are part of the Alpine-Himalayan Mesozoic ophiolite belt. It is a harzburgite sub-type ophiolite and is characterized by thick (~2 km) mafics, tholeiitic basalts, abundant harzburgite now altered to serpentinites. The Bela Ophiolite was formed during the Aptian following Jurassic rifting and was tectoniccally emplaced onto the western margin of Indian plate during the Eocene (Gnos et al., 1998).

Varieties of interesting mineral deposits such as

^{*}Corresponding author. E-mail: ebahmed@yahoo.com. Fax: 92-21-9261330.

The aim of the present contribution is to present the results of a study of the geology, petrology, mineralogy and geochemistry of the ultramafic rocks and serpentinites in Nal and Kurku areas. This work was conducted to elucidate the origin and tectonic setting of these rocks. Geochemical, XRD and petrography data are used to demonstrate characteristics of ophiolitic ultramafic rocks and associated magnesite deposits.

ANALYTICAL TECHNIQUES

Chemical analysis was carried out using an AAS (Hitachi Model, Z-5000). The magnesite samples were also analyzed using a Bruker D-8 Advance X-ray diffracto-meter, Cu and K- α radiation. Thin sections of ultramafic rocks were studied using Laborlus Pols microscope and photographed on Leica Microsystem, (DFC 280) camera model twain 6.6.0.

GEOLOGY OF THE AREA

The study area (Figure 1) lies within the western fold belt of Pakistan. The belt represents the foreland fold and thrust belt along the western margin of the Indian continenttal plate. The belt includes the Bela Ophiolite and sedimentary rocks ranging in age from Jurassic to Miocene (Khan, 2003). Bela Ophiolite is a part of the regional ophiolitic belt ranging from European Alps to Zagros Mountains of Iran to Himalayas.

The Mesozoic Gondwanaland ophiolites exposed in the Alpine-Himalayan orogenic belt shows the progression of an age from the Jurassic in the west to the Cretaceous in the east. Ophiolites associated with superplume events are widely distributed over the globe, although concentrated in mobile belts or at continental margins. Their compositions constrain their petrogenesis to back-arc or suprasubduction zone (SSZ) settings (Vaughan and Scarrow, 2003). The SSZ ophiolites are generated in consistent multi-stage tectonic events (rift, drift, emplacement etc) which are reflected in the heterogeneity of the composition of ophiolites (Shervais et al., 2004).

The geochemistry of the Neotethyan suprasubduction zone encompasses both MORB and island-arc tholeiite (IAT) compositions (Dilek et al., 2007). The SSZ ophiolites that formed in back-arc basins have gross similarities in composition to MORB (Shervais, 2001). Ahmed (1993), Arif et al. (1997) and Gnos et al. (1998) based on geochemical studies showed that Bela Ophiolite formed in MORB setting has signatures of SSZ. The work of Slovenec and Pamić (2005) and Garfunkel (2006) on the Neotethyan ophiolites strengthened such findings.

Gnos et al. (1998) based on Ar isotopic study, showed that the ophiolite formed around 70 Ma. Intraoceanic

subduction initiated between 70 and 65 Ma obduction onto the Indian passive margin occurred during the formation of the Deccan traps at \approx 66 Ma and final thrusting onto the continental margin ended in the early Eocene (\approx 50 Ma). Ophiolite emplacement occurred during the counterclockwise separation of Madagascar and India-Seychelles that caused shortening and consumption of oceanic lithosphere between the African-Arabian and the Indian-Seychelles plates.

The emplacement of the Bela Ophiolite occurred in two steps, first step was the intra-oceanic subduction while the second step was the emplacement of ophiolite onto the western Indian continental margin sediments. Thar formation witnessed the process of emplacement where as Nal Limestone of Oligocene age was deposited after the completion of obduction (Khan, 2003).

Ophiolite exposed near Nal and Kurku areas represents the northernmost extremity of Bela Ophiolite. The rocks are highly disrupted and dismembered and lack a coherent ophiolite sequence. In the study area, the Nal sequence exhibits an abruptly discordant northeastsouthwest trend between the Khuzdar and Nal areas (Figure 1) which is caused by rotation from the drag due to reactivation of east-west trending transcurrent faults associated with a fossil rift to the east (Zaigham, 1991).

Here, the exposures of ophiolite are scarce and dismembered on both sides of the Ornach-Nal fault (Figure 1). The ultramafic rocks of the study area are dominated by harzburgite, dunite, gabbros and serpentinite. Veins of magnesite and pods of chromite are associated with the ultramafic rocks of the study area (Kazmi and Abbas, 2001).

ULTRAMAFIC ROCKS

Petrography

The ultramafic rocks of the study area are serpentinized after harzburgite and are complicated to study. The process of serpentinization is also common in other ophiolites of Central Alps in which relics of harzburgite are still visible in mesh texture of serpentine (Li et al., 2004). In some cases, the serpentine minerals retain the geometric configuration of the original mafic minerals, serpentine that developed as an alteration after olivine has a mesh texture while that formed after orthopyroxene has a bastite texture (Azer and Khalil, 2005). The relatively fresh sample of harzburgite (BB1) of the study area has shown modal composition as enstatite 73%, diopside 8%, olivine 14%, talc 3%, chromite 1% and serpentine 1%. The other harzburgite samples (KK2, KK7, etc.) are intensively serpentinized. These samples are medium to fine grained rocks showing mesh structure (Figure 2a). Their assemblage includes mainly serpentine as well as variable percentages of chlorite, actinolite, talc, brucite and calcite. Relict olivine, orthopyroxene, clinopyroxene and chromian spinel are also present. Serpentine also occurs as



Figure 1. Regional geological map of Khuzdar-Bela area. Figure B shows geology of the study area and sampling sites (Modified after, Gnos et al., 1998).

occurs as thin rims surrounding primary spinel (Li and Lee, 2006). Cryptocrystalline magnesite appears as a coproduct with serpentine, concentrated in the veins. In some rocks, few grains of olivine and subhedral phenolcrysts of pyroxene are present in a fine gro-undmass of serpentine. In many samples, the olivines and pyroxenes retain some relict features of unserpentini-zed protolith. The rims of the olivine grains are altered but commonly the cores are unaltered. These olivine relics are surrounded by serpentine (Figure 2b). Pseudomorphs of prismatic pyroxene are commonly altered to acicular actinolite and fibrous serpentine (bastite; LN2 and BB7). Fine aggregates or foliated masses of talc are present as an alteration of serpentine.Talc also is present as a seconddary vein filling mineral. Talc along with bastite is



Figure 2. Photomicrographs of host rocks of Nal and Kurku areas. Sample No. is given at the top left; crossed nicols. All scale bars correspond to 1 mm.

a common alteration product of orthopyroxenes (Baronnet and Boudier, 2001) (Figure 2).

The opaque minerals in the serpentinites are primarily chromite and magnetite (Figure 2c). Brown chromite/picotite forms tabular and elongated crystals with rounded rims and shows zonation with dark cores and reddish brown rims (Figure 2a). In some rocks, very small opaque globules of chromite are evenly distributed.

Karipi et al. (2006) indicate the presence of high Cr-rich olivine in the SSZ related harzburgite that is also exhibited in the Bela -Ophiolite. Both primary and secondary magnetites are common in serpentinites (Ghoneim et al., 2003). Fe released from the olivine-lizardite interface process of serpentinization facilitates the growth of magnetite (Baronnet and Boudier, 2001).

Magnetite occurs as euhedral-subhedral fine grains, highly corroded and replaced by silicate minerals. Shearing and faulting obliterate the primary textures, forming microfractures in the rock body. These micro-fractures are filled with magnesite/talc. Iron oxide is also present



Figure 3. TAS diagram showing the characters of host rock of the study area. Solid arrows mark the trend of crystal fractionation and broken arrow represents degree of partial melting.

as fine fracture filling. Yellowish, isotropic grains and brownish staining of limonite/hematite can be seen in patches, formed after the alteration of magnetite locally. Veins of calcite network crosscutting the serpent-tine are observed (Figure 2d). Some of these secondary calcite veinlets have stylolitic behavior.

A smaller subset of samples (KK3 and KN1) shows ves-tiges of primary silicate minerals and is intensively altered. Sample KK3 is a fine, lineated, mylonitized rock.

Silicification and sericitization are the dominant processses beside mylonitization. Late stage tectonism gives rise to mylonitic, cataclastic and brecciated textures (Azer and Khalil, 2005). The rock consists of bands of equidimentional small, sutured silica/quartz, fine, flaky serecite as irregular bands, small epidote granules and fibrous actinolite-tremolite band/vein. Probably the formation of epidote and amphiboles in the veins is the consequence of retrograde metamorphism (Guilmette et al., 2005). A network of secondary veinlets of sutured silica grains is very common (Figure 2e). These veins are often developed along pre-existing mylonitized zones.

Rock KN1, is strongly altered into very fine aggregates. Besides these, some mafic rocks are also present in the study area. Sample NL1 is a medium to fine grained oligoclase basalt porphyry. It is composed of laths as well as medium sized grains of oligoclase and augite (Figure 2f). The grains of augite have hourglass texture, are rarely altered at the boundary into brown hornblende and have symmetrical extinction. The groundmass consists commonly of microlites of plagioclase, fine interstitial anhedral pigeonite and small grains of brown hornblende.

Geochemistry

The chemical data presented here and the discussions that follow are based on recalculations using anhydrous data (Hollocher, 2007). In general, harzburgites show depletion in some incompatible major elements (Ca, AI and Na) relative to the average primitive composition of upper mantle (Allegre et al., 1995). The content of these elements in the samples of the studied rocks has hybrid values. Calcium is much higher than the expected values but shows an inverse relation with Mg.

Possibly some of this Ca might have been lost during serpenttinization (Arif and Moon, 2003). Iron also shows loss during serpentinization. According to McDonough and Sun (1995), the content of Ni in primitive upper mantle is >1890 mg/kg while samples of the study area carry comparably low values with an average of 1363 mg/kg. Other trace elements (Ti, Mn, Cu, Co etc) also illustrate variable values. The heterogeneity in the composition of ultramafic rocks is possibly the reflection of complex tectonic processes operative at the mid-oceanic spreading centers.

Furthermore, multi-step hydrothermal alteration processes (serpentinization) strongly modify the composition of the rocks.

The total alkalis and silica relationship are decisive to interpret the characteristics of rock in terms of crystal fractionation and trends of increasing alkalis with increasing SiO₂. Figure 3 illustrates that most of the host rocks are tholeiitic in nature that is in accordance to Sarwar (1992); Ahmed (1993); Arif et al. (1997); Gnos et al. (1998). In the basic magma, the alkaline elements behave as incompatible, so crystallization of Mg and Ferich phases tends to cause both SiO₂ and alkalis to increase (Nelson, 2007). In addition, the host rocks of the study area show increase in the degrees of partial melting (Figure 3) within tholeiitic trend. The magmatism at Reunion hot spot generates tholeiitic magma due to mantle plume activity (Siddiqui et al., 1996; Gnos et al., 1998), suggesting SSZ origin of the Bela Ophiolite (Figure 3).

On an AFM diagram (Figure 4), the samples plot in the field of metamorphic peridotites and ultramafic rocks of ophiolitic affinity (Coleman, 1977). However, a few are plotted close to E-type MORB. This is the trend that would be expected from fractional crystallization involving the removal of early crystallizing olivines and pyroxenes from a tholeiitic basaltic liquid (Nelson, 2007) (Figure 4).

Magnesium number is a significant tool to distinguish the members of ultramafic rocks. The orthopyroxenites are clearly distinctive compared with the websterites and clinopyroxenites. Overall, the orthopyroxenites are characterized by high Mg-number ranging from 83 - 92 (Berly et al., 2006). The majority of the ultramafic rocks and their serpentinite equivalent in the study area have a range of Mg# 97.5 - 82.6 with an average of 91.39 (Table 1), suggesting primitive mantle compositions. The differrentiation index (DI) is a measure of differentiation of magma. Basalts generally have a low differentiation index (<25). The samples of study area have DI between 0.7 -7.7, however sample # BB7, LK1 and KN2 have respecttively higher values (Table 1).



Figure 4. AFM diagram representing trends of magmatic crystallization among the host rocks of the study area (modified after Coleman, 1977 and Nelson, 2007).

Table 1. Important factor for the evaluation of
ultramafic rocks of the study area. Calculations
are after Hollocher (2007).

Sample #	Mg #	DI	Density	Temp. ℃
BB1	90.5	0.3	3.18	1386
BB3	88.9	7.7	3.28	1348
BB6	88.9	0.8	3.34	1385
BB7	91.2	38.2	2.77	1410
KK2	97.5	1.7	3.19	1227
KK3	93.7	6.7	3.12	1309
KK7	91.5	7.6	2.74	1196
KN5	91.9	3.1	2.81	1286
LK1	88.5	46.4	3.02	1290
LK2	97.4	1	3.18	1391
LK4	92	1.9	3.32	1376
LN1	91.3	1.3	2.81	1283
LN2	93.6	1	3.25	1226
KN2	82.6	54.2	2.99	1338

The suprasubduction zone ophiolites are generally characterized by enrichment in large ion lithophile elements ridge is disturbed. At this stage, a high input of water generates low Ti (boninitic) magma (Hoeck et al., 1999) and addition of mobile element (K) in magma. The event of SSZ in the study area can be visualized in the form of Ti vs. K plots. The diagram (Figure 5) show variable



Figure 5. K vs. TiO₂ Diagram showing two distinct populations.

concentration of Ti and K in the samples. At the time of formation, these rocks are high in Ti and low in K. During SSZ stage, Ti shows depletion and K enriches in the rocks. In some area where the spreading zone and subduction zone interferes, generated magma shows similarity with MORB-type. This is in accordance to earlier workers Ahmed (1993); Arif et al. (1997); Gnos et al. (1998). The remnant of arc is not observed, probably the evidences are destroyed during large-scale strike-slip displacement as it happens in Alaska (Amato et al., 2007).

MAGNESITE

The XRD analysis of six selected samples revealed magnesite as the major mineral having MgCO₃ 99.7 - 82%. Sample BB2 shows the presence of hydromagnesite as the main constituent. Hydromagnesite is formed during serpenttinization as the bi-product of brucite and other Mg-bearing minerals. It is important to note that sample LK3 has aragonite as the second most abundant mineral. It occurs as a secondary component in altered ultramafic rock in association with hydromagnesite, brucite and magnesite.

Ghoneim et al. (2003); Zedef et al. (2000) pointed out the formation temperature of hydromagnesite \approx at 300 °C. The presence of hydromagnesite associated with magnesite in the study area confirms the above temperature range.

Different carbonate minerals (calcite, aragonite and dolomite) are commonly allied with the formation of magnesite of ultramafic origin. In the study area, aragonite is reported in association with magnesite while in contrast, the southern part of the ophiolite belt contains calcites



Figure 6. Compatibility of trace elements with Mg ion in magnesites of the study area.

and dolomites (Bashir et al., 2004 and Khan, 1998).

Trace elements can be used to reflect the mineralogy of carbonate rocks, although the documented references are scanty (Dickson, 1990). The occurrence of trace elements in different carbonate lattice (calcite, dolomite, aragonite and magnesite) largely depends upon ionic size, charge, abundance and coefficient of distribution. Magnesium has a prime role in the lattice of magnesite. However, the substitution of these trace elements into the lattice of magnesite is limited and most commonly occurs as impurities (Schroll, 2002).

The difference of ionic size of Mg and other trace elements vs. their mutual relationships as correlation

Coefficient of the studied rocks shows some interesting results (Figure 6). During magnesite formation, the majority of trace elements were expelled from the crystal lattices into two distinct trends. Trend I evolution due to the variation in ionic radii difference among the elements of interest. The expulsion increases with the increase in the ionic radii difference (Ca>Cr>Fe>Co). The removal of other transition elements (Trend II) depends upon the nature of elements rather than ionic radii. The intensity of removal is found more for Zn> Ni >Cu >Co (Figure 6). Manganese is the only element that shows slight positive correlation (r=0.043), probably because of its amphoteric nature. Potassium in spite of maximum ionic radii difference has good compatibility in contrast to Na which has r = -0.225 (Figure 6).

Ghoneim et al. (2003) and Rösler and Lange (1972) have used Cr/Mg, Fe/Mg and Mn/Mg ratios to discriminate different magnesite deposits. The average Cr/Mg, Fe/Mg and Mn/Mg ratios are found to be 1×10^{-5} , 7×10^{-3} and 2×10^{-4} respectively indicating their affiliation with cry-

ptocrystalline Kraubath-type magnesite. The plot Fe versus Mn is also valuable to discrimination between magnesites of different origins (Ghoneim et al., 2003). The Fe/Mn ratio in magnesite is commonly correlated due to the redox behaviour of both metals (Schroll, 2002). All studied samples plot close to the field of cryptocrystalline (Kraubath-type) magnesite (Figure 7).

Conclusions

In the Nal-Karku area, small isolated outcrops of ultramafic rocks in association with gabbroic and doleritic suits are the northern extension of Bela Ophiolite and are part of the Alpine-Himalayan Ophiolite Belt of Cretaceous age.

Petrography and mineralogy reveals that the studied rocks are serpentinites after harzburgite containing variable proportions of olivine and pyroxene relics.

Orthopyroxene (enstatite) is the dominant pyroxene whereas clinopyroxene (diopside) is less abundant. Variable amounts of chlorite, magnetite, actinolite, talc, brucite and calcite are also present. Serpentine commonly occurs as angular and medium sized fragments, exhibits mesh texture and occur in veins.

The rocks have high Mg and SiO_2 indicating that harzburgite was the original protolith. On an AFM dia-gram, the protolith appears as metamorphic period-tites and ultramafic rocks of ophiolitic affinity. The plots on TAS diagram signify increase in the degrees of partial melting. High Mg# 97.5-82.6 and low values of differentiation index (0.7-7.7) also suggest primitive mantle compositions. The low content of Fe, Al, Ca, Mn, Na and K



Figure 7. Fe vs. Mn contents in the studied magnesite, compared to cryptocrystalline (Rösler and Lange, 1972) and sparry magnesite (Martiny and Rojkovic, 1977).

suggests that elements were removed during serpenttinization.

Differential replacement of Ti and K demark influx of water during the process of serpentinization. Magnesite samples are poor in Fe and Mn. The average Cr/Mg, Fe/Mg and Mn/Mg values reveal that the studied magnesites are genetically affiliated with cryptocrystalline Kraubath-type magnesite.

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