APPLICATION OF GEOCHEMISTRY TO EMERALD EXPLORATION IN SWAT, PAKISTAN

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ABSTRACT

There are very few cases in the world where geochemistry has been used for emerald exploration. The present studies to find out geochemical pathfinders for emerald mineralization in Swat are hence significant.

Geochemical characteristics of the emerald bearing rocks of Swat Emerald Mines have been determined. For this purpose rock and stream sediment analyses of mineralized and non-mineralized areas are carried out using Induced Couple Plasma Emission Spectrometry.

Univariate and multi-variate studies on the analytical results of 105 rock and stream sediment samples of Swat Emerald Mines and Malam area were carried out. These studies reveal that high Be along with high Li, Sr and La may be taken as pathfinders for emerald mineralization in the Swat Emerald Mines.

Malam was selected as target area where talc-carbonate have the same physical and mineralogical characters like that of the Swat Emerald Mines. In this area no significant anomalies could be distinguished using the geochemical model of Swat Emerald Mines, however, high Be and Li anomalies are evident in Malam stream sediments. Such geochemical studies, if carried out in conjunction with mineralogical and structural studies of a particular area, would be more helpful for pinpointing its emerald mineralization.

INTRODUCTION

Emerald is the most important gemstone of Pakistan and it has the major share in foreign exchange earnings from gemstones. Its economic potential appears to be significant since it is mineralized at a number of places along a linear belt of about 400 km. These deposits are either pegmatitic or pneumatolytic and hydrothermal in nature (Hussain, 1988).

Mining in Swat district is being carried out presently at three places, i.e. Mingora, Gujar Kili and Khazana (Shamozai). The former two mines are controlled by the Gemstone Corporation of Pakistan. The newly discovered Khazana emerald deposit is being mined by the Private Sector.

The emerald mineralization in Swat appears to be the product of low temperature hydrothermal solutions which acted on carbonate-bearing altered ultrabasics, the latter providing the necessary chromium for emerald mineralization. The emeralds are concentrated along faults and fractures together with gangue calcite and quartz (Kazmi et al., 1986).

In the present studies samples of talc-carbonate rock and stream sediment from Swat Emerald Mines and Malam have been analyzed. It was intended to characterize the mineralized and barren rocks of Swat Emerald Mines for the purpose of emerald exploration in Malam area.

GEOLOGY OF THE MINGORA AREA

The Mingora area (Kazmi et al., 1984) is structurally composed of three tectonostratigraphic groups of rocks from north to south:

i. The Kohistan arc sequence, which has been thrust over
ii. The Indus suture melange group, which in turn has been obducted on to
iii. The Indian sub-continent sequence
The latter two are significant for the emerald mineralization.

The Indian subcontinent sequence

It comprises four lithostratigraphic units. The Precambrian Manglaur schist is the oldest and intruded by Swat granite gneiss (early Paleozoic). Both of them are folded into an antiform. The Alpurai schist is composed of siliceous schist and calcareous quartz-mica-garnet schist; it lies probably unconformably on top of Manglaur schist and Swat gneiss and is overlain by Saidu calc-graphite schist. The upper part of Saidu schist has been overthrust by the Indus suture melanges comprising an imbricate zone.

The Indus suture melange group

This comprises fragmented blocks derived from oceanic crust, volcanic arcs, trenches and continental margins ranging from Precambrian(?) to late Cretaceous in age. The melange is divided into three sub units by Shangla, Makhad and Charbagh-Kishora thrusts. From north to south these are Shangla blueschist melange, the Charbagh greenschist melange and the Mingora ophiolitic melange. Northward the Kohistan sequence overrides all of these units.

GEOLOGY OF THE MINGORA EMERALD DEPOSIT

The Mingora emerald deposit spreads over an area of about 180 acres at the northern margin of Mingora (Fig. 1). At the mines, from west to east, the following tectonostratigraphic sequence is exposed:

Charbagh greenschist melange Thrust Mingora ophiolitic melange Thrust Saidu calcareous graphitic schist

Emerald mineralization is confined to the Mingora ophiolitic melange. This unit is composed of, in decreasing order of abundance, tectonized blocks of serpentinite, talc-magnesite schists, greenstone metabasalt, greenschist metapyroclastics, metagabbro, metasediments and metachert. All of this is set in a matrix of talc-chlorite-magnesite schist and scanty calcareous quartz-mica-chlorite schist. Three main features distinguish this melange from the other two: (a) abundance of ophiolite suite of rocks, (b) presence of talc-magnesite schist, and (c) emerald mineralization.

EMERALD MINERALIZATION

The emerald mineralization of Mingora area is non pegmatitic and is commonly associated with one of the following features;

i. Faults and fractures.

ii. Limonite zones.

iii. Calcite nodules and veinlets.

iv. Quartz veins and stockworks.

At the Mingora deposit the following four distinct modes of emerald occurrence are present.



Fig. 1. Geological map of Swat Emerald Mines, Mingora (After Kazmi et al., 1986).

i. Disseminated emerald mineralization along shear zone

This type of mineralization is characteristic of the central quarry of Mine 2. The host rock is composed of sheared talc-chlorite-magnesite schist with talc-rich and magnesite-rich layers and lenses. Mineralization occurs between two parallel normal faults along a shear zone which has been limonitized and contains a few scattered quartz veins. In this zone emerald crystals occur in sporadically scattered pockets or nests 5 to 15 cm across. Smaller crystals are disseminated throughout the matrix of the mineralized zone. The emerald is commonly associated with fuchsite and tourmaline.

ii. Emeralds in fracture filling along narrow limonitized joint planes or fault planes

In the northern and southern quarries of Mine 2 the shear zones, faults and joints of the host rock are filled in by limonite and veinlets or stringers of quartz and calcite. Emerald mineralization is mainly confined to limonitized fault and joint planes. Better production is obtained from a point where two mineralized fractures intersect. Emerald crystals also occur in quartz and calcite along the fracture. This type of deposit has yielded stones of good quality and size though the production tends to be sporadic.

iii. Emeralds associated with stockworks

Mine 3 of the Mingora deposit contains intensely fractured magnesite filled with stockworks of quartz which contain emeralds in association with fuchsite and tourmaline. Emeralds from such deposits are commonly of lighter colour.

iv. Emerald along tension gashes

At the Islamia trench of Mine 1, large tension gashes have been filled in by quartz lenses in the talc-chlorite-magnesite schist. Emeralds occur in a 15 to 30 cm thick layer of talcose rock surrounding the quartz lenses. Large euhedral emerald crystals of good deep green colour and clarity have been obtained from such deposits.

EMERALD EXPLORATION

Until late seventies emerald exploration in the world had been carried out without the use of modern scientific methods. Discovery of new deposits took place either by chance or it resulted from the efforts of prospectors who carried out digging at some apparently promising rock. Very little has been reported about emerald exploration, except in Colombia (Beus, 1979) and Zimbabwe (Bohmke, 1982; Chikohara, personnel communication). In Colombia geochemical techniques were successfully applied for the emerald exploration in Cordillera Oriental (Beus, 1979). Besides, distribution of beryllium in stream sediments of Oslo, Norway, has been described by Brinck (1965). Debnum et al. (1960) and Debnum (1961) also carried out geochemical prospecting studies in Zimbabwe and Uganda and found significant Be anomalies around beryllium pegmatites.

In Pakistan efforts for the exploration of gemstones including emerald started in 1980 when the Gemstone Corporation of Pakistan (GEMCP) initiated different exploration programmes. Very little attention was paid to establish the geochemical characterization of Swat Emerald Mines which could be of help in exploration in that region. GEMCP, however, sent some samples for analysis in various laboratories around the country. The high detection limits of a number of trace elements including Be could not provide the desired results.

A collaborative project between GEMCP and UNDP was undertaken during 1985-87. In this project geochemical studies were carried out on a few rocks and minerals of talc-carbonate schist. However, its main emphasis was on the use of cathodoluminescence for exploration purpose (Mariano, 1985). Since it was already proved (Kazmi et al., 1986; Jan et al., 1981) that emerald mineralization in Swat, besides structure, is lithologically controlled, it was considered that Malam talc-carbonate schists, situated at about 25 km NE of Mingora, in the ophiolitic melange (Hussain et al., 1982; Kazmi et al., 1984) having lithological and mineralogical characters similar to those of Swat Emerald Mines may be a suitable prospective target for emerald exploration using geochemical techniques.

SAMPLING TECHNIQUES

A total of 17 and 8 rock samples of mineralized and non mineralized talc-carbonates respectively from the Swat Emerald Mines, Mingora were collected (Fig. 2). The samples from the mineralized zones did not have any visible emerald crystal. The samples from non-mineralized zones were taken from the close vicinity of emeraldbearing zones as well as up to tens of meters away from the mineralized zone to see the variation in elemental distribution of these rocks. Each sample weighing about 1 kg was taken from the fresh rocks except in highly sheared areas where deep weathering has affected the rocks.

Rock sampling from the talc-carbonates of Malam area was done on a regular interval of about 200m (Fig. 2). Areas with rocks other than talc-carbonates and highly weathered talc-carbonates were excluded in sampling to avoid any misleading results.



Fig. 2. Location map of rock and stream sediment samples of Swat Emerald Mines, Mingora and Malam area.

A total of 16 stream sediment samples were collected from the Swat Emerald Mines (Fig. 2). Most of the streams in the mine area cut a variety of rocks including talc-carbonates. Very few streams cut only the talc-carbonates forming the dominating rock type. The streams cutting the mineralized zones but having the contamination of mine debris were not sampled. Each stream sediment sample weighed about 100 gm.

Twenty nine stream sediment samples have been collected from Malam area. During sampling each stream cutting talc-carbonate was sampled. However, from longer streams more than one samples were taken with an interval of about 200m.

The majority (about 70% to 90%) of the sediments from each stream of Swat Emerald mines and Malam had grain size distribution in the range of -10 to +80 mesh. The +10 mesh material was ignored and the remaining part was further ground to obtain -80 mesh for analytical work.

METHODS OF GEOCHEMICAL ANALYSES

In the present studies the induced couple plasma (ICP) emission spectroscopic method with ability to rapidly determine 25 elements has been used. The samples were dried for a couple of hours before crushing. The crushing was done in agate mortar and pestle and the crushed material was sieved to 80 mesh. The -80 mesh samples were decomposed and analyzed.

Fusion (with lithium metaborate) and acid (nitric-perchloric and hydrofluoric) decomposition methods were tried on 12 rock samples of Swat Emerald Mines and Malam. On the basis of ICP results the acid decomposition method was selected. The reasons were:

i. Lower detection limits in acid digestion, for instance the detection limit of Be is eight times lower than the other method.

ii. The upper detection limits are also high in the acid decomposition method which helps make a better comparison of major elements.

iii. The lithium metaborate method detects 21 elements whereas by acid digestion method 25 elements can be determined.

iv. Only acid decomposition method allows the analysis of some of the important trace elements like Li, Rb, Mo, Cd and Pb.

v. Accuracy and precision of analytical results of reference material and samples were comparable in both the cases.

RELIABILITY OF THE GEOCHEMICAL ANALYSES

For proper analytical control (Rose et al., 1980) duplicates of the samples (10%), reference material (6%) and reagent blank (5%) have been added. In reference material about 80% elements showed a variance of up to 3% of the actual value. In five replicates of stream sediment samples the average percentage covariance of the elements (except Be and Pb), comes to a maximum of 8.73. In case of Be and Pb it is 10.31% and 15.90% respectively. In rock samples the six replicates show percentage covariance up to 10 in case of Li, Na, Be, Mg, Ca, Sr. Al, Cr, Mn, Fe, Co, Ni and Zn. All this indicates quite a high precision of these analysis. K, Rb, Mo, Ag and Cd are below detection limits.

52

STATISTICAL INTERPRETATION OF THE RESULTS

Statistical interpretation of the analytical results was done using an advance computer programme. In the first stage, the behavior of each element was studied in the mineralized and barren rocks of the Swat Emerald Mines and their comparison was made with talc-carbonates of Malam area. Similarly distribution patterns of different elements in stream sediments of Swat Emerald Mines and Malam were compared. The distribution pattern of some of the major and trace elements could be used in discriminating the mineralized and barren zones of the Swat Emerald Mines.

In the 2nd stage multivariate statistical analyses (Davies, 1986) were carried out on the analytical results of the rocks and stream sediment samples of Swat Emerald Mines. The purpose was to reveal the geochemical processes involved with the emerald mineralization on the basis of different element associations. Based on the results of the Swat Emerald Mines, an attempt was made to find out any probable emerald mineralization in the Malam area.

UNIVARIATE ANALYSES

Rock samples of the Swat Emerald Mines and Malam

A comparison of the major and trace element distribution in the mineralized and barren rock samples of Swat Emerald Mines and those of Malam is shown in Fig. 3. The mineralized rocks in Swat Emerald Mines are comparatively high in Be, Li and Sr and depleted in Cr and Zn. These mineralized rocks are also high in Ca, Al and V than the barren rocks. Mg is however lower in former than the latter.

In Malam area five samples are anomalously high in Be and Li as well as in K, Ba, Al, La, V, Cr, Ti, Mn, Fe, Cu, P, Zn, and Co. These samples are comparatively depleted in Mg, Ca and Sr. The samples showing this chemical signature represent the south- western part of the Malam talc-carbonate body. Deep intense weathering effects on these rocks may be due to their sheared nature as they lie close to a major fault.

Although apparently weathered rocks were excluded in sampling yet the high contents of lithophile, chalcophile and siderophile elements in some of the talc-carbonates of Malam area might be attributed to the deep weathering effects not visible to the naked eye (Rose et al., 1980).

The rock characteristics related to a few important trace element distribution which are generally associated with the acidic environments as well as beryllium mineralization (Staatz et al., 1965) are described below. These elements are also anomalously high in the mineralized talc-carbonates of Swat Emerald Mines.



Fig. 3. Plots of different elements in talc-carbonates of Swat Emerald Mines and Malam area.



Fig. 3 (continued)



Fig. 3 (continued)

56

Lithium

The average and standard deviation (S.D.) in 17 samples from the mineralized zone of Swat Emerald Mines is 13.89 ppm and 14.42 ppm respectively. The highest Li bearing samples are from Mine 1. In barren rocks, the average of Li is 4.97 ppm. It is below detection limit in 2 samples. In Swat Emerald Mines, Li is about 3 times higher in the mineralized rocks than in the barren rocks and high Li is always associated with the emerald mineralization.

In Malam area, only 4 samples contain higher Li contents than the barren rocks of the Swat Emerald Mines (Fig. 3). In these samples, Li ranges from 12.45 ppm to 47.50 ppm. The overall average of Li in the Malam area is 7.52 ppm with a S.D. of 8.12.

Beryllium

Beryllium in 17 samples from the mineralized zone of Swat Emerald Mines ranges from 0.15 ppm to 1.85 ppm with an average of 0.63 ppm. In barren rocks Be is below detection limit in one sample. One sample from the barren zone contains 1.40 ppm Be. This sample is from a zone which in the past has shown some indications of emerald mineralization but on the basis of some excavation, the zone could not be proved as a mineralized one. Excluding this sample, the other samples from the barren zone have an average of 0.23 ppm with standard deviation of 0.159 ppm.

Distribution of Be in Malam and Swat Emerald Mines is shown in Fig. 3. Sample nos. MM38, MM49, MM50, MM51 and MM54 have comparatively the highest Be contents (from 0.52 ppm to 0.82 ppm) which are comparable with the high Be-bearing samples of the mineralized zones of Swat Emerald Mines. The rest of the samples from Malam area are very low in Be, ranging from 0.1 ppm to 0.22 ppm.

Strontium

It ranges from 1.05 ppm to 129 ppm with an average of 23.42 ppm in the samples from mineralized zone of Swat Emerald Mines. Comparison of the rock samples from Swat emerald Mines (Fig. 3) reveal that the mineralized rocks have about 4 times more Sr than the barren rocks. The higher Sr is almost always found associated with the emerald mineralization.

In Malam area, Sr does not have any positive correlation with Li and Be. The Sr average in Malam samples is 20.00 ppm with S.D. of 25.7 ppm.

In talc-carbonates of Swat Emerald Mines Li, Be and Sr may have been derived from the mineralizing fluids. High Ni, Co and Cr contents in SEM and Malam rocks are, however, typical of ultramafics (Goles, 1967) and confirm that talc-carbonates are the altered product of ultrabasics/ultramafics (Jan, 1968; Chaudhry et al., 1980).

Based on the above observations it is clear that the distribution pattern of some of the major and trace elements can be used to distinguish the mineralized and barren rocks of the Swat Emerald Mines.

Stream sediments of Swat emerald mines and Malam

The samples which best represent the uncontaminated stream sediments of Swat Emerald Mines are anomalous in Be and Li. Other elements which are high in these samples are Pb, La, Ba and K. Rb is detected in only two stream sediment samples which represent the mineralized zone.

In Malam Stream sediments a number of samples have higher Be, Li, Pb, La, Ba and K than stream sediments from the mineralized zone of Swat Emerald Mines and do not indicate any potential emerald mineralization.

MULTIVARIATE ANAL'ISES

After doing univariate analysis it was felt that to uncover the underlying processes and major and trace element associations, it was necessary to carry out multivariate analysis such as Principal Component Analysis (Davies, 1986). For this purpose the following data sets were selected to compare the chemical characteristics of rock and stream sediments of Swat Emerald Mines and then to apply the same on Malam area to find out any emerald mineralization.

- i. Mineralized and barren rocks of Swat Emerald Mines
- ii. Malam talc carbonates.
- iii. Stream sediments of Swat Emerald Mines
- iv. Stream sediments of Malam area.

Cumulative variance of principal component loadings of rock and stream sediment samples of Swat Emerald Mines and Malam area have been shown as Fig. 4. Based on the univariate analyses, as well as the chemical formula of emerald (Be₃Al₂Si₆O₁₈) it was assumed that high Be is an essential component of an emerald indicating anomaly. Therefore the loadings showing high Be were selected and analyzed in all the sampling groups. The geochemical behavior shown by the selected principal loadings (Fig. 5) are described under different sampling groups.



Fig. 4. Plots of cumulative percentage variance of principal component loadings of rock and stream sediment samples.

Mineralized and barren rocks of Swat emerald mines

In the case of Mineralized and barren rocks of Swat Emerald Mines, principal component loadings 1, 6 and 7 (Fig. 5) have been selected. The study of PCL1, which accounts for 28.80% of the total variance, revealed that the major elemental relationship in the mine area is represented by high Be along with high Li, Sr, Ba, Al, Ti, V and Zn. The samples (4 nos.) which show the highest score are from the mineralized zone of Mine 1. Two more loadings show significant high Be with other elements. PCL6 represents 5.16% of the total variance. In this case high Be goes with high Pb, Zn and La and low Cu, Fe and V. This relationship is represented by four samples from the mineralized zone. Two barren samples also show the same trend but have comparatively low score. High Be along with high Sr and Li is shown by one sample from Mine 1







Fig. 5 (continued)

and two samples from Mine 2. This association is shown by PCL7 and accounts for 4.93% of the total variance. In these samples Mn, Zn and P have negative correlation with Be, Sr and Li.

Rock samples of Malam area

The study of the PC loadings of Malam rock samples (Fig. 5) shows that in 6 samples high Be is associated with high K, Ba, La, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Ag, Zn and P. This relationship is shown by PCL1 and accounts for 46.51% of the total variance. These geochemical characters are comparable with the mineralized rocks of SEM except the presence of high Be which is low in these Malam samples. Although the above samples contain high Be, yet the low Li contents and the presence of high Mn, Be, Ni and other elements indicate some weathering effects on these rocks. PCL4 represents 6.86% of the total variance. Be is slightly high with high Ba, Mo and Mo. Li and V have negative correlation in the four samples representing this association. No other loading shows high Be in case of Malam talc carbonate samples. Three other loadings have been considered worth mentioning because of their high Li and/or high Sr with moderate or low Be as Li and Sr almost always indicate the emerald mineralization in Swat Emerald Mines. PCL2 which represents 11.14% of the total variance shows another association with high Li, Na, Ca, Sr and Mo and low Ni and Mg. These characters are comparable with the mineralized rocks of Swat Emerald Mines except the presence of high Be which is low in Malam samples. PCL6 represents 4.26% of the total variance. In this case Be is moderate along with Li and P and low Cu, Ca and Sr. Mn is also low in these samples. The two samples which have high score come from places far away from each other in Malam area. PCL5 shows high Li, Sr and Mo with



Fig. 6. Plots showing contribution of different elements in PC loadings of stream sediment samples of Swat Emerald Mines and Malam area.

low Na, Ca and Pb. This loading accounts for 6.35% of the total variance. Be is comparatively low in 3 samples which show high score.

Stream sediments of Swat emerald mines

As mentioned earlier the stream sediments from Swat Emerald Mines were not collected from the places which were considered to be contaminated by the mined material. In the case of stream sediments PCL2 (Fig. 6) represents 15.76% of the total variance. This loading shows high Be along with high Ba, La, K and Li. The maximum score is shown by 4 samples. In PCL4 high Be ia associated with high Pb, Rb, Ag and Mo. Its share of the total variance is 4.50%. Four samples have the highest score including one sample from a stream which cuts the barren rocks only. In PCL6 high Be, Li and Zn go together and accounts for 10.87% of the total variance. PCL7 (1.87% variance) also indicates the association of high Be and Li in the same sample. On the basis of these loadings it may be concluded that the stream sediments representing uncontaminated mineralized zones of SEM are generally high in Be and Li. Ba, La and K are also high in these samples.

Stream sediments of Malam

In Malam area only two loadings have significant eigen values (Fig.6). PCL1 accounts for about 40% of the total variance. In this case there is a relationship of high Be and high Li, Ma, K, Al, Ti, Mn and P. The six samples which represent this relation ship are widespread. This geochemical pattern is not understood. High Be along with other high elements may be due to adsorption by Mn (Rose, 1980). High Be and high Ba, Rb, K and La relationship is shown by three samples. This association is represented by a loading (PCL2) which accounts for 24.70% of the total variance. Four Other samples show similar character but have low score. Manganese is also low in these samples. Rock samples of these areas are high in Be, K, Ba, Al, La, Ti, V, Mn and Fe. These rocks are considered to have been affected by weathering.

DONDLUSIONS

The following conclusions are made from this study:

1. Emerald mineralization in Swat Emerald Mines is non-pegmatitic. In such deposits the mineralized rocks do not provide any pronounced physical characters which might help in emerald exploration. 2. Until now, emerald exploration in Pakistan has been carried out without the application of geochemistry. The present studies were carried out on 105 rock and stream sediment samples from Swat and Malam areas. The geochemical characters of the rock and stream sediments of Swat Emerald Mines were then applied to the Malam area to find out any hidden emerald mineralization.

3. These studies reveal that Be along with Li seem to be significant pathfinders. Associated trace elements, however, vary to some extent in Mine I and Mine II of the Swat Emerald Mines.

4. The rock samples of Mine 1 of Swat Emerald Mines show different elemental associations than those of Mine 2. In the Mine 1 area, the samples from Farooq and Islamia Mines show high Be with high Li, Sr, Ba, Al, Ti, V and Zn. Most of the samples from the mineralized zone of Mine 2 have high Be with high La and P. The PC analyses of the mineralized rocks only indicate the association of high Be with La in the north and south faces of Mine 2. Based on these studies it can be inferred that there are two different geochemical processes responsible for emerald mineralization in Mine 1 and Mine 2.

5. The rock samples from the southwestern part of the Malam talc-carbonate body have high Be, K, Ba, Al, Ti, V, Mn, Fe, Co, Ni, Ag and P. These rocks are comparatively low in Li and Sr. In Malam, while sampling, the uppermost weathered talc-carbonate cover was removed and apparently fresh looking rocks were sampled. But it appears that the anomalous quantities of the above mentioned elements including Be are probably due to deep weathering effects on Malam talc-carbonates.

6. The present study of the stream sediments of Malam area does not provide a clear picture about any possible emerald mineralization. High Be is present in a number of samples which represent a wide area. Be may be contributed in the stream sediment by the breakdown of beryl having Be as a major element. High weathering effects on the Malam rocks can be a reason for high Be contents in a number of stream sediments.

7. For optimum results in cases where chemical characteristics of rocks of two areas are to be compared, the use of geochemistry requires comprehensive and thorough studies at a large number of fresh samples or having strictly comparable weathering effects.

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