Genesis of tourmalinite from Chitral, Northern Pakistan

MOHAMMAD ZAHID¹ & CHARLIE J. MOON² ¹Department of Geology, University of Peshawar, Peshawar, Pakistan ²Department of Geology, University of Leicester, Leicester, UK

ABSTRACT: Miniki Gol scheelite-bearing tourmalinite occurs within the Jurassic Arkari Formation. The Arkari Formation is located near the Pak-Afghan border within the Eastern Hindu Kush and is composed of garnet mica schist, phyllite, marble, mica quartzite, calc-silicate quartzite and subordinate tourmalinite. The extension of tourmalinite is very limited and has been identified at three locations within the mica schist. Tourmalinite is dominantly composed of tourmaline, spessartine-rich garnet, quartz and scheelite. Tourmaline reaches up to 80% by volume in some tourmalinites. The chemical composition of tourmaline and garnet of the tourmalinite fairly corresponds with those of the nearby exposed leucogranite

The values of K_2O , MnO, Zn, Rb and Ba of Miniki Gol tourmalinite, are not markedly different from the associated schist and thus cannot be considered as siliceous chemical precipitates (exhalites). The limited extension of the tourmalinite is also inconsistent with the occurrence of exhalites. The lack of Sb, Hg, Ag, F and P in the tourmalinite also rules out the possibility of the exhalative activity in the study area.

A linear relationship between LREE and elements of obvious igneous origin such as Zr, Hf and Be in the tourmalinite indicates a post-magmatic metasomatic activity. The Miniki Gol leucogranite can be considered as potential source for the extreme enrichment of boron in the tourmalinite.

INTRODUCTION

Arkari Formation hosts the subordinate scheelite-bearing tourmalinite and is composed of garnet mica schist, phyllite, marble, mica quartzite and calc-silicate quartzite (Fig.1). Garnet mica schist and phyllite are the dominant rock types in the study area (Fig. 1). Tourmalinite is defined by Slack (1982) as containing 15-20% or more tourmaline by volume, whereas the Miniki Gol tourmalinite contains up to 80% tourmaline by volume. Miniki Gol tourmaline-rich rock can be divided into three subgroups. The first type occurs in lensoid mass, which is spatially associated with discordant quartz veins. The second

most widespread type is the and tourmaline-bearing schist interlayered with mica schist. The third variety, tourmalinite has been found as small pockets within the tourmaline-bearing schist at three locations around 2km strike length. According to Leake et al. (1989) the studied tourmalinite is not laterally extensive and have sharp contacts with adjacent rocks. The scheelitebearing tourmalinite is concentrated within the mineralised zone about 400 meters away from the exposed leucogranite (Fig.1). It is composed of tourmaline, spessartine-rich garnet (over 40% by volume), quartz and manganifeous ilmenite together with traces of magnetite, pyrite and pyrrhotite.



Fig. 1. Simplified geological map of the Miniki Gol and surrounding area.

Schistosity is well developed in the tourmaline-bearing schist and as well as tourmalinite. Tourmaline needles and blades occur within the foliation but without alignment of long axes, whereas garnet occurs as almost subhedral crystals. Both garnet and tourmaline contain numerous inclusions, which according to Leake et al. (1989) may define a planar fabric. Scheelite occurs as fine-grained disseminated grains as well as lenses. Deformation phases (D1) and (D2) are well developed in the tourmalinite.

The present paper focuses on the genesis of tourmalinite on the bases of mineral chemistry of tourmaline, garnet and the geochemistry of the tourmalinite.

GEOLOGY OF THE MINIKI GOL AND SURROUNDING AREA

The study area is located within the eastern Hindu Kush approximately 50km to the northwest of the Northern suture zone. The Hindu Kush extends southwest from the Pamirs and passes into Afghanistan and northwestern Pakistan, where it merges with western Karakoram at Tirich Mir. Pudsey et al. (1985) described the stratigraphy and geology between the Pak-Afghan border and Northern suture (in the Chitral and surrounding area) and divided it into two tectonic units, the Northwestern unit and the Central unit.

The Central unit, which lies between the Fault and Northern suture Reshun predominantly of Paleozoiccomposed Mesozoic metasediments. This unit comprises Gahiret Limestone, Koghozi Greenschist, Chitral Slate and Shoghor Limestone from south to north in the Chitral and surrounding areas. The Jurassic Northwestern tectonic unit extends northwestwards from Reshun Fault to the Pak-Afghan border and probably to the

Pamirs (Pudsey et al., 1985). This unit comprises mainly metapelite intercalated with mica quartzite and calc-silicate quartzite. These rocks have undergone at least two phases of deformation with Sloverprint foliations and S2 penetrative foliations as well as F1 and F2 folds (see Fletcher, 1985). Metamorphism within the formation is highly variable ranging from lower greenschist grade through garnet-staurolite schist to sillimanite grade followed bv the emplacement of Miocene leucogranite. Leake et al. (1989) separated the metasediments to the northwest of Shoghor Limestone into three lithostratigraphic Formations, Sewakht, Lutkho and Arkari Formations. The latter two are probably subdivisions of the Lun Shales which overlies the Shogram Formation in the Tirich and Mastui valleys as described by Hayden (1915) and Talent et al. (1982). The Sewakht Formation, that lies the Krinj Limestone, adjacent to is characterised by greenschist, micritic limestone, cherts, ferruginous dolomitic carbonate, phyllite, sandstone and breccia. This sequence probably correlates with the Shogram Formation of Devonian age, however, in the type locality Shogram Formation is composed predominantly of limestone and sandstones (Leake et al., 1989). A major tectonic break to the northwest, delineates Sewakht Formation from the monotonous sequence of light green phyllite of Lutkho Formation. This is followed by Arkari Formation that extends up to the northwest of the Tirich Mir pluton.

MINERAL CHEMISTRY

Tourmaline

The chemical analyses of the tourmaline from tourmalinite and leucogranite are plotted on the Al-Fe-Mg diagram of Henry and Guidotti (1985) (Fig.2). The analysed tourmaline falls along the schorl-dravite solid solution join (Fig. 2), covering a wide Fe-Mg range. The

negative correlation between the FeO and MgO corresponds to the schorl-dravite solid solution series. Except few analyses of the tourmaline from tourmalinite, the majority analyses of the tourmaline of the leucogranite and tourmalinite fall in the field of metapelite (Fig.2) on the Al-Fe-Mg diagram of Henry and Guidotti (1985). The composition of the tourmaline from studied leucogranite is markedly different from the Fe-rich schorl, which is considered as typical tourmaline related to felsic plutonic rocks (Slack, 1982). This could either be considered as xenocrysts contaminated from the wall rock or alternatively, indicate the pelitic character of the leucogranite.

Garnet

Garnet occurs as almost subhedral crystals in tourmalinite and contains numerous inclusions. The analysed garnet in leucogranite and tourmalinite is spessartine-rich almandine with up to 16.62 wt% and 16.04 wt% MnO, respectively.

Compositional zoning is observed in the garnet of tourmalinite in contrast to the lack of specific zoning pattern in the garnet from leucogranite. MnO in the garnet of tourmalinite generally increases from core to margin with marginal depletion of FeO.

Plotting the Miniki Gol garnet data on an Mn-Mg-Fe triangular diagram (Fig. 3) show



Fig. 2. Miniki Gol tourmaline compositions in terms of oxides and cations: (A) Cations proportions of Al, Fe (total) and Mg superimposed on the compositional fields (1-6) of Henry & Guidotti (1985); (1) Li-rich granitoid pegmatites and aplites (2) Li-poor granitoids and their associated pegmatites and aplites (3) Fe³⁺-rich quartz-tourmaline rocks (Hydrothermally altered granites) (4) Metapelites coexisting with Alsaturating phase (5) Metapelites not coexisting with Al-saturating phase (6) Fe³⁺-rich quartz-tourmaline rocks, calc-silicate rocks and metapelites.

that with the exception of a few analyses from tourmalinite, the analyses fall within the compositional field of the igneous garnets defined by Miller and Stoddard (1981). Moreover, garnet analyses from the two-mica granite and tourmalinite at Miniki Gol plot above the line of 20 mol% spessartine (Fig.3). This is the lower limit reported for two-mica granites by Miller and Stoddard (1981). Except for the Ca content, which is higher in tourmalinite, garnets from Miniki Gol leucogranite and tourmalinite are similar in composition.

The proposed tourmalinite is significantly different from the Broken Hill tourmalinite by containing high amount of wt% Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O and low value of SiO2 (Table 1). This difference can also be noticed in trace elements as the Miniki Gol tourmalinite contains high levels of W, Sn, B, Li, Be, Sr, Cr and low levels of F, Cl, As, Ba, Rb, Th, Y, Zn and Pb relative to that of Broken Hill (Table 1).



Mn

Fig. 3. Composition of Miniki Gol garnet in terms of Mn, Mg and Fe (atomic proportions), showing the compositional field of igneous garnets defined by Miller and Stoddard (1981).

GEOCHEMISTRY

Major and trace elements analyses of the Miniki Gol tourmalinite are presented in the Table 1 and compared with the exhalative scheelite-bearing tourmalinite of Broken Hill, Australia, (Slack et al., 1993). The chemistry of the tourmalinite shows high levels of MnO, Fe_2O_3 and low value of K_2O compared with the schist and calcsilicate quartzite. The Mn and Fe concentrations are high in those samples, which contain abundant (relatively spessartine-rich) garnet. High K_2O content is

Sample		Min	Max	Mean	N	Broken Hill•
SiO		46.8	61.7	51.2	12	58
TiO ₂		0.7	1.5	1.0	12	0.93
Al ₂ O ₂		21.0	29.5	23.7	12	21.31
*Fe-O		6.3	13.3	9.8	12	7.6
MnO		0.0	2.6	1.1	12	0.12
MgO		2.3	4.5	3.1	. 12	1.86
CaO		0.3	3.7	2.0	12	0.39
Na _o O	× 28	1.0	3.3	1.7	12	0.94
K-0		.0.1	3.1	0.9	12	1.23
P.O.		0.0	0.2	0.1	12	0.12
Total		90.9	96.0	94.5	12	6. K
			Trace elem	ents in ppm		
В		9310	14800	11827	10	7455
F		790	1350	1070	8	2800
CI		40.0	70.0	50	8	335
S		0.0	280	110	8	
As		0.7	2.4	1.4	9	73.15
Li		37.7	. 172	. 80	13	39.28
Be		2.8	13.7	6.5	13	1.92
Cs		4.0			1	10.46
Ba		4.9	720	204	13	330
Rb		1.1	187	51.8	13	148.7
Sr		200	520	300	13	71.7
Th		255	41.6	17.5	13	34.3
TI		3.0	5.8	4.6	7	6 34
7.		106	323	170	13	213.4
LIF		2.0	6.0	3.2	5	5.8
Ta		1.1	1.5	13	3	5.8
1a Nh		1.1	22.1	18.6	13	24.57
NO		4.9	33.1	21.4	13	24.57
I C-		- 11.5	44.9	19.2	13	19.24
SC		11.5	20.2	10.5	13	10.24
v o		102	200	142	13	107.7
Cr	201	102	200	142	13	15 16
Co	1.1	10.2	29.7	20.5	13	15.10
NI		. 11.7	40.2	30.5		20.20
Cu		1.4	20.2	120	12	14.28
Zn		97	155	150	13	2048
Ga	8).	21.7	42.2	27.0	13	50
Pb		16.7	39.0	24.8	13	23.33
w		0.3	7830	1760	13	80
Sn	1530	3.8	23.1	13.21	13	22.5
Mo.		0.0	1.1	0.5	10	
Sb		0.3	1.7	0.9	4	0.19
La	55	16.0	42,0	27.3	. 8	69.0
Ce		31.0	78	55	8	128.7
Nd		16.0	39.0	24.9	. 8	51.97
Sm		3.9	6.5	5.1	. 8	11.81
Eu		0.5	1.0	0.7	8	1.3
Gd		1.0	2.0	1.3	3	1
Tb		0.6	2.7	1.4	5	1.61
Yb		1.6	2.5	2.0	8	4.06
Lu		0.2	0.4	03		0.6

* = Total iron expressed as Fe_2O_3 ; Std = Standard deviation; N = Number of samples; • = Mean analyses of Broken Hill tourmalinite (after Slack et al., 1993). Be and Li were analysed by ICP-ES and B, Cs, U, Hf, Ta, Sb and REE by INAA. All the other elements were analysed by XRF.

reported in the muscovite-bearing tourmalinite. Tourmalinite in the area of under consideration is also high in B, Be, Sn, in addition to W and low in Li, Ba, Rb and REE compared with Miniki Gol schist. Apart of these elements the geochemistry of the Miniki Gol tourmalinite and schist is similar.

Tungsten contents in the Miniki Gol tourmalinite are highly variable and range from few ppm to 0.8%. No correlation has been observed between W and elements such as Sn, Li and Be in the tourmalinite. Similarly, tungsten shows no relationship with the Zr and elements of possible exhalative character such as B and F. In contrast, F and B show positive correlation with each other (r=0.3). Similarly, Rb and Ba show a strong positive correlation with each other (Fig. 4A) and both these elements are depleted in the proposed tourmalinite. The Rb and Ba in these rocks are probably accommodated in the plagioclase and muscovite. It is interested to note that the concentrations of elements such as P and F which might indicate an exhalative activity (Sonnet et al., 1985; Plimer, 1984, 1987), are almost the same as found in the associated schist. The levels of Hg and Ag in the tourmalinite are also low (less than 1 ppm). These evidences are against the possibility of the precipitation of tungsten as scheelite during the exhalation at the Miniki Gol area as suggested by Leake et al. (1989).

REE pattern

The REE abundance of the tourmalinite is presented in Table 1 and Fig 4B. The REE pattern shows a LREE enrichments having La/Yb ratios generally greater than 10. Gd in most of the samples is below detection limit and if present, is very low in these rocks. A strong correlation exists between La and Ce which reflects a similar geochemical behaviour during the regional metamorphism and hydrothermal alteration (Fig. 4C). Like other units in the study area, La and other

LREE also display a linear relationship with elements of obvious igneous origin such as Zr, Hf and Be (Fig 5A-C), possibly indicate a post-magmatic hydrothermal activity. However, an inverse relationship has been found between La and W (Fig. 5D), whereas no relationship exists between REE and boron. The REE contents are quite different from the Broken Hill tourmalinite (Table1) of exhalative origin. The Broken Hill tourmalinite is rich in REE content as compared to the tourmalinite in the study area and also HREE in the Broken Hill are slightly elevated relative to LREE (Slack et al., 1993). Moreover the Broken Hill exhalite and tourmalinite display both prominent positive and negative Ce anomalies (see Lottermoser, 1989).

DISCUSSION AND CONCLUSION

The striking feature of the Miniki Gol tourmalinite is its association with scheelite mineralisation. In comparison, scheelite is not associated with tourmaline-bearing schist at Miniki Gol. Moreover, tourmaline is concentrated only in schist at Miniki Gol and decrease towards the Garam Chashma away from the Miniki Gol. Tourmaline is almost rare or absent elsewhere within the schist at the study area. The limited strike length of the tourmalinite and its concentration in the vicinity of leucogranite (Fig.1) might indicate a genetic relationship between these two rocks.

The Miniki Gol tourmalinite contains up to 3.1% K₂O, up to 190 ppm Rb, up to 700 ppm Ba, up to 2.6% MnO and up to 150 ppm Zn. These levels are not markedly different from the associated schist (see also Zahid, 1996) and thus can not be considered as siliceous chemical precipitates (exhalites) as suggested by Leake et al. (1989). The high content of MnO is due the presence of abundant spessartine-rich garnet. It should also be noted that the background levels of







Fig. 4. (A) Linear relationship between Ba and Rb. (B) Chondrite-normalised REE pattern of tourmalinite. Different symbols indicate different samples (C) Relationship between La and Ce.





Fig. 5. Relationship of La (ppm) with (A) Zr (ppm), (B) Hf (ppm), (C) Be (ppm) and (D) with W (ppm) in tourmalinite. The same relationship holds for other LREE elements.

W in the Miniki Gol metasediments are slightly higher than those of the average shale (Turekian & Wedepohl, 1961), and therefore do not support the pre-granitic enrichment of tungsten. The very low levels of Sb. Hg, Ag, F and P in the tourmalinite are not compatible to the exhalative activity in the study area. In contrast, the linear relationship between LREE with Zr, Hf and Be in the tourmalinite indicates a magmatic or postmagmatic metasomatic activity. However, the positive correlation between B and F may signify a pre-metamorphic cogenetic relationship. The differences in the REE abundances of the Miniki Gol tourmalinite and the Broken Hill tourmalinite of exhalative origin also minimize the chances of the possible exhalative activity in the study area.

An evaporitic-sabkha model for the Miniki Gol tourmalinite can easily be ruled out as lack of evidence for the presence of evaporite.

A boron-rich clay is also an inadequate precursor, as clay minerals are not known to contain more than 2000 ppm of boron (Slack et al., 1984). This amount of boron would only be sufficient for 9% tourmaline by volume (Plimer, 1986), whereas Miniki Gol tourmalinite contains up to 80% tourmaline by volume.

Miniki leucogranite Gol can be considered as a potential source for the extreme enrichment of boron. The chemical composition of the tourmaline of the tourmalinite is similar to that of the leucogranite and therefore indicates a genetic linkage between these two rocks. The consistency of spessartine-rich garnet both in tourmalinite and leucogranite further establishes a genetic link between these widespread occurrence rocks. The of spessartine-rich garnet and its concentration in the tourmalinite (up to 50%) also reflect

extensive Mn-rich hydrothermal activity in the Miniki Gol area. The reverse trend with rims richer in MnO than the core in the garnet of the tourmalinite reflects falling temperature during retrograde metamorphism and corresponds to a metasomatic origin (Deer et al., 1982).

REFERENCES

- Deer, W. A., Howie, R. A. & Zussman, J., 1982. Rock-forming minerals, orthosilicates. Vol. 1A, Longman, London.
- Fletcher, C. J. N., 1985. Gold, antimony and tungsten mineralisation in the Chitral District, Northwest Frontier Province, Pakistan. Unpublished report for Sarhad Development Authority, Peshawar.
- Hayden, H. H., 1915. Notes on the geology of Chitral, Gilgit and the Pamirs. Ind. Geol. Surv. Records, 45, 271-235.
- Henry, D. J. & Guidotti, C. V., 1985. Tourmaline as a petrogenetic indicator mineral: an example from the staurolite grade metapelites of NW Maine. Am. Min., 70, 1-15.
- Leake, R. C., Fletcher, C. J. N., Haslam, H. W., Khan, B. & Shakirullah. 1989. Origin and tectonic setting of stratabound tungsten mineralisation within the Hindu Kush of Pakistan. J. Geol. Soc. London, 146, 1003-1016.
- Lottermoser, B. G., 1989. Rare-earth element study of exhalites within the Willyama Supergroup, Broken Hill Block, Australia. Mineral. Deposita, 24, 92-99.
- Miller, C. F. & Stoddard, E. F., 1981. The role of manganese in the paragenesis of magmatic garnet: an example from the Old Woman-Piute Range, California. J. Geology, 89, 233-246.
- Plimer, I. R., 1984. The role of fluorine in the submarine exhalative systems with special reference to Broken Hill, Australia. Mineral. Deposita, 19, 19-25.
- Plimer, I. R., 1986. Tourmalinites from the golden dyke dome, Northern Australia. Mineral. Deposita, 21, 263-270.
- Plimer, I. R., 1987. The association of tourmalinite with stratiform scheelite deposits. Mineral. Deposita, 22, 282-291.

- Pudsey, C. J., Coward, M. P., Luff, I. W., Shackleton, R. M., Windley, B. F. & Jan, M. Q., 1985. Collision zone between the Kohistan arc and the Asian plate in NW Pakistan. Trans. Roy. Soc. Edinburgh, 76, 463-479.
- Slack, J. F., 1982. Tourmaline in Appalachian-Caledonian massive sulphide deposits and its exploration significance. Trans. Inst. Min. Metall. (Sect. B: Appl. Earth Sci.), 91, B81-B89.
- Slack, J. F., Herriman, N., Barnes, R. G. & Plimer, I. R., 1984. Stratiform tourmalinites in metamorphic terranes and their geologic significance. Geology, 12, 713-716.
- Slack, J. F., Palmer, M. R., Stevens, B. P. J. & Barnes, R. G., 1993. Origin and significance of tourmaline-rich rocks in the Broken Hill District, Australia. Econ. Geol., 88, 505-541.

- Sonnet, P., Verkaeren, J. & Crevola, G., 1985. Scheelite bearing calc-silicate gneisses in the Provence crystalline basement (Var, France). Bull. De Min., 108, 377-390.
- Talent, J. A., Conaghan, P. J., Mawson, R., Molloy, P. D. & Pickett, J. W., 1982. Intricacy of tectonics in Chitral (Hindu Kush): faunal evidence and some regional implications. Geol. Surv. India Miscel. Pub., 41, 77-101.
- Turekian, K. K. & Wedepohl, K. H., 1961. Distribution of the elements in some major units of the earth crust. Geo. Soc. Am. Bull., 72, 175-192.
- Zahid, M., 1996 Genesis of stratabound scheelite and stratiform Pb-Zn mineralisation Chitral, Northern Pakistan, and its comparison with S-W England tin-tungsten deposits. Unpubl. Ph.D. thesis Univ. Leicester.