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New observations of Tin Mineralization Potential Vis-à-Vis Ore Petrographic, Alteration and Geochemistry in the Southeastern part of Bastar Craton, Central India

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Abstract

The Tin mineralizations occur around the Katekalyan area, hosted in the acid magmatic rocks. The evolution differentiating granitic magma shows residual melt enrichment where end products intruded as pegmatites into the rocks. The different kind of pegmatite occur as simple unzoned, recrystallized (granitic pegmatite), and metasomatic greisenised and albitised pegmatites which emplaced within the pre-existing rocks of metabasic intrusive, granite (KG), granite gneiss (KGG). Sometimes it also found in metasediments as mineralised and non-mineralised characters along the fractures and foliation planes trending N-S, E-W and more frequently are observed NNW-SSE trends. Cassiterite is most important Tin-ore mineral and associated with pegmatites. Some cassiterite samples exhibit colourless to brown shades zoning which indicate multi stage growth. The cassiterite samples contain significant amounts of Sn, Nb, Ta with minor W.

The partial melting model shows that the variation 5 to 50% partial melting of bulk continental crust for KG as well as KGG rocks but bulk distribution coefficient for Sr (DSr) shows low i.e. <<10. The upper limit of partial melting of bulk crust estimates ~50 % for KG and KGG rocks are consistent with required rheological, critical melt percentage to leave the source region has decreased granite melt which were capable to mineralised tin ore elements. It is interesting to note that the SnF_4 and $SnCl_4$ probably not stable in presence of water under geologically reasonable conditions.

Keywords: Tin-mineralisation, cassiterite, Katekalyan, Bastar Craton, Central India

1. Introduction

Ore petrography is studied on polished ore section which is always difficulties mainly due to their hardness, variation in mineral and ore composition. The Bastar area is known for a potential zone of metallic and non-metallic deposits. Previous workers have taken special attention to deposits in different part of the craton special references to the Kondagaon and Bhopalpatnam areas (Mishra et al., 1984, 1988), Sukma- Konta-Dantewada area (Ramakrishanan, 1990). The detailed geological, structural and petrological works in Bastar Craton have carried out by Babu (1983) and Ramesh Babu et al. (1984, 1993). Singh and Singh (2011) stated that tin-bearing granitoids of the acid magmatic rocks namely biotite granite (KBG), tourmaline granite (KTG), hornblende granite (KHG) and also granite gneiss (KGG) have special significance to their possible mineralization episode of the Katekalyan area, Bastar Craton.

The authors have selected opaque sections studies with suitable sized ore samples, and put to coarse-grinding on steel plate using 200-400 and 600-mesh carborandum powder followed by fine grinding in similar way on glass plate using 800-mesh powder. In the next stage some finer grinding was done by dry method, using 2/0, 3/0, 4/0 and 5/0 emery polishing papers. After this, the specimens were subjected to polishing by chrome oxide powder followed by alumina or synthetic diamond paste for about 3 hours. The precautionary measures were strictly taken in such cases during alumina or diamond polishing was done very slowly but with uniform light pressure. Therefore, integrated approach as ore petrographic, alteration and geochemistry used to determination of Tin mineralization in South-Eastern part of Bastar Craton, central India.

2. Geological Setting

In Peninsular India, the SE-part of the Bastar Craton surrounded by the Eastern Ghat granulites on the east, Bailadilla Iron ore Group of rocks to the west, high grade metamorphics of Sukma Group in the south (Fig. 1). The volcano-metasediments rocks occur in studied area belong to Bengpal Group (Babu, 1983). Narainpur, Indravati

and Sabri Group of rocks occurring as isolated basins of sediments unconformable are overlying the igneous complex (Fig. 1). The regional geological map with radiometric age data of the tin mineralized belt in parts of Bastar Craton is given in Fig. 1 from published literature.

The Bengpal metasediments found as enclaves in the basement gneisses and migmatitic rocks whereas the granites occur as discrete unites within the gneisses association with the supracrustal rocks. The gneissic-migmatite complex constiuting more than 65% of the Bengpal metamorphites and is similar to the Peninsular Gneissic Complex of South India. The Katekalyan area consists of andalusite sericite schist, quartz-sericite schist, banded magnetite quartzite, grunerite-magnetite quartzite, metabasic intrusive and metabasic extrusive rocks (Singh et al., 2011).

The NNW-SSE trends with steep northerly dipping granite show gneissosity characteristics in the area. Three phases of deformation related to granitic activity have been noticed (Murthy et al., 1982). The first phase F1 is along ENE-WSW to E-W followed by F2 along NNE-SSW to NW-SE and the last F3 along N-S to NNE-SSE. The granitoids (KG and KGG) have been subjected to subsequent pneumatolytic and hydrothermal alteration viz; microclinisation, albitisation, greisenisation and sericitisation are more prominent.
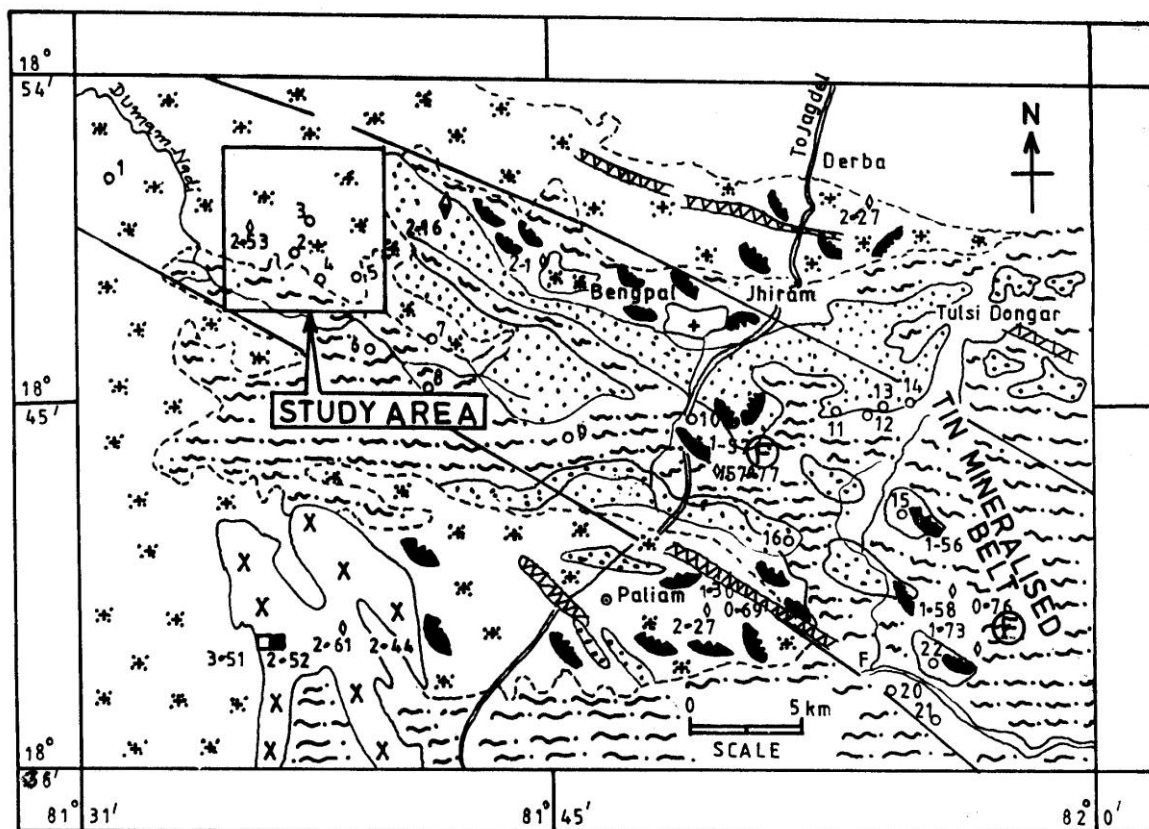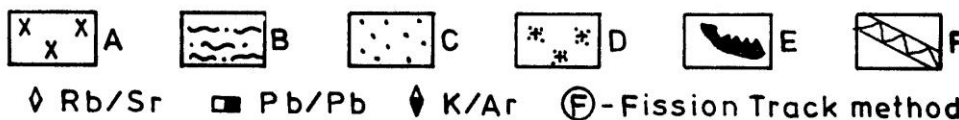

Fig. 1. Location map of the study area and regional geological map with radiometric dates (billions of years) of the primary tin mineralised belt in the southeastern part of Bastar Craton, central India. (**A**): Sukma Supracrustal Suite, (**B**): Bengpal Metasediments, (**C**): Metabasic Intrusives, (**D**): Stanniferous Granite complex, (**E**): Mineralised Pegmatites, (**F**): Silicified Shear Zone. **Locality:** 1. Metapal 2. Katekalyan 3. Kopanar 4. Kondaras Dongri 5. Pinjupara 6.Parcheli 7. Koapal 8.Bothapara 9. Marjun 10. Tongpal 11. Chidpal 12. Chuirwada 13. Bedanpal 14. Bodawada 15. Govindpal 16. Kudripal 17. Jongarpal 18. Mundwal 19. Pushpal 20. Kikripal 21. Bondey 22. Mundaguda.

3. Mineralisation potential of the area

The Tin mineralizations occur around the Katekalyan area, hosted in the acid magmatic rocks. The evolution differentiating granitic magma shows residual melt enrichment where end products intruded as pegmatites into the rocks. The cassiterite is mainly associated with columbite, tantalite, lepidolite, beryl and fluorite which may point out that niobium, tantalum, lithium, beryllium, fluorine and rare earths were intimately involved in the transportation of tin from magmatic to pneumatolytic stage.

The younger intrusive type of coarse-grained non-foliated porphyritic biotite granite characteristics of third type phase of tin-bearing pegmatites, which occurring in the pre-existing granitic gneiss. The biotite granite at

Lokharas area is soda-rich (fine-grained aplitic nature) concentrated 50 ppm Sn whereas the porphyritic leucogranite having 100 ppm of Sn near Katekalyan village which indicates that stanniferous nature of the granite (Murthy et al., 1982). Occurrence of discrete cassiterite crystals especially in the unzoned pegmatites can be related to the pegmatitic phase of acid magmatism. The enriched tin-bearing pegmatites occur in meta-basic rocks. However, for the first time pegmatite with discrete crystals of cassiterite have been found emplaced within granite at Kondaras Dongri and Benglur areas. In the greisenised pockets portion of the pegmatites where the tourmaline (boron-metasomatism), fluorite and rare minerals of niobium and tantalum generally associated with cassiterite bearing pegmatites. The post-magmatic metasomatic process form pegmatites due to actions of chemically active aqueous solutions and volatiles, where the tin has been fixed in the lattice of rock forming minerals subsequently remobilized and reconcentrated for tin ore mineralisation.

4. Microscopic observations

Optical characters of the ore minerals in the polished ore sections were studied with the help of a polarising ore microscope (Carl Zeiss, Jena, the then G.D.R.) and consulted standard work of Ramdohr (1969). The preliminary observations of the ore samples reveal that cassiterite was the most abundant tin ore mineral in Katekalyan area. The other associated ore minerals like columbite, tantalite, tapiolite, microlite and wolframite were also identified in small amount. Limonite (mainly goethite) was the common secondary ore mineral, and was recognised as the alteration products. The gangue minerals associated with the ore are quartz, fluorite, zinnwaldite and K-feldspar. The texture and structure of the ore and their petrography distinguish it into two main classes, namely primary and secondary ore minerals with the salient features are given below.

4.1 Primary ore minerals

4.1.1 Cassiterite (SnO_2, Tetragonal):

Cassiterite is most important ore mineral associated with pegmatites in the studied area which occurs as coarse disseminated grains with euhedral to subhedral shape, bypyramidal form and massive in nature. The mineral is dark gray to black in colour with grayish to brown streak and greasy to admantine lustre. It shows brownish grey to light grey in colour and have pitted (poor polishing) to non-pitted surface in reflected light. The internal reflection colour (Fig. 2a) shows distinct anisotropism from light grey to dark grey and a brick red to yellow pale brown due to its numerous inclusions and impurities to its high tantalum and iron content in the lattices. Twinning was noted as common feature in many sections but zoning was not distinct, may be because of the strong internal reflection. Cassiterite is easily distinguished from columbite-tantalite by its micro-hardness, poorly polished sections, cracks and crevices and low reflectivity (brownish gray). In polished sections of cassiterite, two sets of very feeble cleavage traces have been observed only under cross-nicols (Fig. 2a). Exsolution texture among cassiterite, columbite-tantalite and tapiolite is a common phenomenon and helpful in the understanding the genesis of mineralisation. The intensity of the colour of cassiterite is lower than that of associated columbite-tantalite.

Few cassiterite samples exhibit zoning from colourless to brown shades (Fig. 2a) indication of multi stage growth. The colourless zone is free from any inclusion whereas the reddish brown and brownish red shade zone contains numerous inclusions possibly of Ta-W-bearing phases. The paragenetic relationship suggest that the bright coloured (unzoned/inclusion free part) that is Ta-free cassiterites were crystallised first which is followed by the dark crystallization of coloured Ta-Sn rich zones during the lowering of temperature. The coarse grains of cassiterite are usually fractured which are filled by the quartz and columbite-tantalite minerals (Fig. 2b).

4.1.2 Columbite-tantalite {(Fe, Mn) (Ta, Nb)$_2$O$_6$, Orthorhombic} :

Columbite-tantalite is usually present in minor quantities, as inclusions in cassiterite but occasionally it occurs as separate mineral. The exsolved grains of columbite-tantalite (Fig. 2c) are irregular in shape and vary in size from small globules to large lamellar grains. The larger grains of columbite-tantalite are definitely the product of normal intergrowth. The columbite-tantalite minerals show moderate reflectivity (whitish grey) than that of cassiterite, and weak but distinct pleochroism. Columbite/tantalite shows very weak anisotropism and straight extinction. The columbite-tantalite has the solid solution series between columbite (FeMn)Nb$_2$O$_6$ and tantalite(Fe,Mn)Ta$_2$O$_6$ (Babu,1993) and similar view interpret for cassiterite in Katekalyan area.

4.1.3 Tapiolite [(Fe, Mn) (Ta, Nb)$_2$O$_6$ – Tetragonal] :

The tapiolite mineral occur in minor amount, usually associated with cassiterite, showing similar physical properties and makes it difficult to distinguish in the field. Tapiolite mostly occurs as very small grains, bluish grey in colour with brownish tint and characteristics of low reflectivity (Fig. 2d).

The tapiolite, ore petrography is characterized by weak reflection pleochroism (but very distinct in oil). It shows strong anisotropism but generally it is masked by its internal reflection. However, cassiterite distinguished in better polishing, due to its slightly higher reflectivity, lower micro-hardness and moderate anisotropism (Fig. 2e). In general, the paragenetic relation of tapiolite mineral associated with other ores indicates that it has intergrowth with cassiterite or as replacement type texture with the original tin mineral, whereas very rare textural relationship with columbite-tantalite mineral.

4.1.4 Microlite [(CaNa)$_2$ (Ta$_2$O$_6$) (O, OH, F) – Isometric]:

The microlites occur at peripheral part of the columbite-tantalite and might be of the later phase. The microlite (white internal reflection) noticed in the form of irregular, disconnected and randomly oriented patches (Fig. 2f).

4.1.5 Wolframite [(Fe,Mn)WO$_4$ – Monoclinic] :

The tungsten mineral found as inclusions in cassiterite, columbite-tantalite and rarely in tapiolite. It has moderate reflectivity and similar to columbite-tantalite. The wolframite mineral, more grayish white distinguished from whitish gray of columbite-tantalite (Fig. 2c). Moreover, it is having much deeper red internal reflection and sometimes the bladed form with slanting terminations properties distinguished from other opaques. Reflection pleochroism is quite low and can be seen along grain boundaries. The textural study points the presence of tiny inclusions, which suggest that it may be related with early paragenetic sequence than cassiterite.

4.2 Secondary mineral

Goethite is noticed as intergrowth in many samples of cassiterite and other minerals like columbite-tantalite and tapiolite. The fine veins and veinlets of goethite (Fig. 2e), were noticed randomly with tin ore and show grayish reflection colour in reflected light. It also show dull gray to bright gray with a bluish tint variation. The dull gray colour reflection, suggest the iron hydroxide is not fully crystalline.

4.3 Alteration environment

The cassiterite mineral is mainly associated with pegmatites in the later phase of granitic rocks in the Bastar Craton. The cassiterite associated with other metasomatic alteration minerals encountered by the exchange and receives elements from the wall rocks with combined effects of pneumatolytic gases and some aqueous mineralised solutions, which existing the halogen elements, water phosphorus and a few alkali metals.

The different metasomatic activities which leads to the formation of rare metal mineralisation in the craton, reveal four distinct zones of formation of cassiterite along with Nb and Ta mineral compositions, viz, microclinisation (potash-metasomatism), albitisation (soda-metasomatism), greisenisation (pneumatolytic activity) and sericitisation, on the basis of field evidences, petrographic and geochemical studies in the Katekalyan granites and pegmatites.

Source of the alteration solutions is highly debated. The apical zones of tin-bearing granitoids are sites of intense and complex metasomatic activity with the transportation of tin ions leading to the formation of discrete crystals of cassiterite. The albitised pegmatites can be identified by their monomineralic nature, predominant of plagioclase feldspars and sub-ordinate quartz and incipient mica. The feldspar is mostly albite or cleavelandite variety, which were formed by the replacement of microcline indicating the prevalence of albite due to the soda metasomatism. The phenomenon of albite enrichment is accompanied by the presence of disseminated cassiterite rich with minor columbite and tantalite minerals. Greisenisation is represented by the decomposition of feldspars and biotite and by the formation of quartz, mica, topaz and ore minerals in the granite and pegmatite. The OH, F, Li, Sn, W, B introduce and the removal alkalies (especially Na, less pronounced K) are the most significant, while Si, Al remains essentially constant. Greisenised pegmatites constituting mainly of quartz and muscovite intercalations with lepidolite, associated with cassiterite, beryl, tourmaline were formed mainly due to the actions of pneumatolytic activity in the marginal areas of the pegmatites. Muscovitisation of K-feldspar is more intense than plagioclase feldspar due to volatile rich fluid activities. Highly sericitisation of feldspar were observed due to metasomatic hydrothermal fluid activity in the pegmatites. Tourmalisation is also intense at the contact of granites and quartz veins. Wall rocks are composed of tourmaline, muscovite, chlorite, apatite, fluorite and opaque minerals. The mineralisation is associated with wall rock alteration where the intensity of alteration is directly proportional to the degree of mineralisation in the Katekalyan area.

5. Geochemistry of Cassiterite

Eight representative samples of cassiterite have been analysed. Three samples were taken from placer deposits and five samples were selected from mineralized pegmatite zone of the different localities. The analytical data are given in table 1.

The element analyses of cassiterite (Table 1) indicated the admixture of tin as major constituent with subordinate quantities of niobium, tantalum, tungsten, iron, manganese and other trace elements. Tin (Sn) content in the cassiterite ranges from 56.57 to 71.84% indicating that basically 70 to 90% is as SnO$_2$ mineral phase. The niobium metal content ranges from 0.52 to 0.97% whereas tantalum varies from 1.87 to 2.29%. The concentration of tantalum is more than that of niobium content. Thus, on the whole tin, niobium and tantalum concentration constitute more or less 80%. The WO$_3$ varying from 1.83 to 2.58%, FeO (t) ranges from 0.01 to 11.58%; MnO content varying from 2.09 to 7.22%; MgO ranges from 1.99 to 3.79%; TiO$_2$ varying from 0.07 to 0.45% and CaO ranges from 1.16 to 3.98%. Trace elements like Ni, Ga and Rb are present as low in content. Hence, it is evident that a number of metallic cations are known to enter into the solid solution in cassiterite. It is presumed that the presence of Nb, Ta and W will have no effect on the cell dimension of the cassiterite.
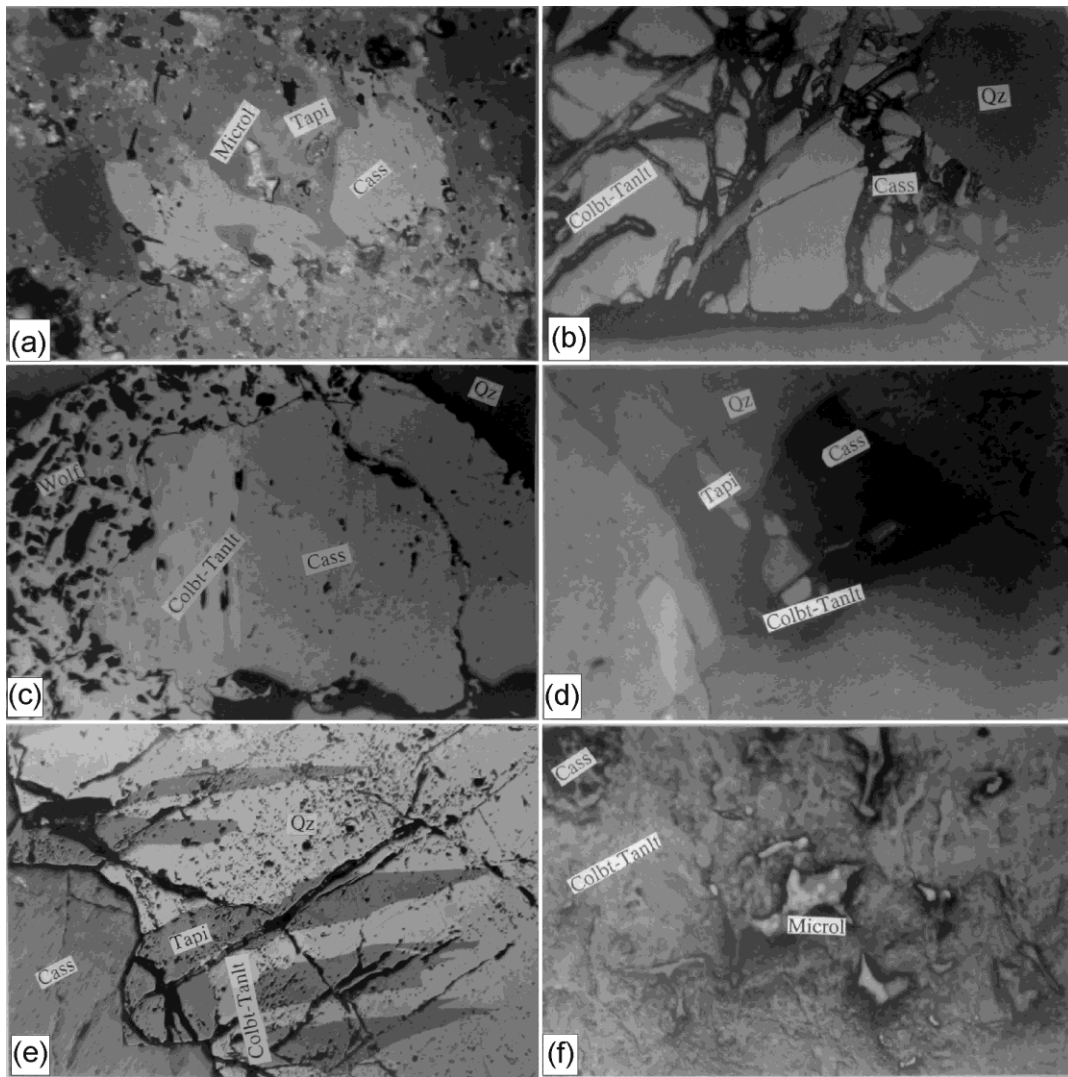
Fig. 2: Shows photomicrographs of ore minerals **(a):** cassiterite mineral shows two sets of very feeble cleavage traces. In the other portions, microlite shows white internal reflection whereas tapiolite gives reddish internal reflection (Reflected Light, 1.6 × 0.32 × 4; Crossed); **(b):** columbite-tantalite (whitish gray) is present in the highly fractured cassiterite crystal and also observed the veinlets of cassiterite (brownish gray) and quartz (dark gray) (Reflected Light, 10 × 7; Uncrossed); **(c):** intergrowth of pitted cassiterite and columbite-tantalite (whitish gray) and the wolframite (grayish white) is present at the contact of cassiterite (Reflected Light, 10 × 7; Uncrossed); **(d):** exsolution texture among cassiterite (brownish gray), columbite-tantalite (white) and tapiolite (brown gray) within the mass of cassiterite (light gray) (Reflected Light, 10 × 7; Uncrossed); **(e):** cassiterite (dark) is showing intergrowth with tapiolite (bright) present as twin lamellae and at the sides of this intergrowth, columbite-tantalite (yellowish cream) appears to replace it and also show the presence of goethite (Reflected Light, 10 × 7; Uncrossed); **(f):** cassiterite (brownish gray) shows the inclusions of columbite-tantalite (whitish gray) and also microlite (white internal reflection) in the form of irregular, disconnected and randomly oriented patches, (Reflected Light, 10 × 7; Uncrossed).

Table 1: Element Analyses of Cassiterite from Katekalyan Area, Bastar Craton, India.

Sample No. Ref./ Spot No.	R89/517 CF/1210	R89/612 CF/1220	R89/790 CF/1230	R89/830 CF/1240	R89/915 CF/1250	R89/1305 CP/5	R89/1399 CP/99	R89/1405 CP/105	Average
Sn (%)	56.57	61.98	60.12	71.84	70.76	63.68	69.78	62.34	64.63
Nb (%)	0.97	0.52	0.89	0.76	0.96	0.79	0.84	0.75	0.81
Ta (%)	2.11	2.29	2.18	1.99	1.87	2.16	2.05	1.89	2.07
WO_3 (%)	2.54	2.48	1.83	2.38	2.46	1.95	2.58	2.19	2.30
FeO_T (%)	11.58	11.49	10.99	11.38	11.27	NA	0.01	0.13	8.12
MnO (%)	7.22	5.86	6.78	7.17	6.86	2.16	2.09	2.38	5.06
MgO (%)	2.13	2.34	2.09	1.99	2.19	3.79	3.69	3.56	2.72
TiO_2 (%)	0.11	0.09	0.14	0.18	0.07	0.45	0.39	0.41	0.23
CaO (%)	1.39	1.28	1.43	1.32	1.16	3.98	3.76	3.57	2.24
Ni (ppm)	16.00	14.00	18.00	13.00	17.00	16.00	15.00	17.00	15.75
Ga (ppm)	42.00	40.00	43.00	41.00	41.00	94.00	89.00	95.00	60.62
Rb (ppm)	53.00	51.00	51.00	54.00	49.00	52.00	51.00	48.00	51.12

Niobium (Nb) and tantalum (Ta) are characteristically oxyphile forming a number of complex minerals. They enter isomorphously into minerals of iron, manganese, titanium, tin, tungsten, uranium, thorium and rare earth

elements. Niobium (Nb) indicates close relationship with titanium, tungsten, thorium and the rare earths of cerium group.

However, Tantalum (Ta) correlates with zirconium, tin, the rare earths of yttrium group, uranium and lithium. Mineral occurring in sodic alkali granites and syenites are generally niobium rich, whereas those in lithium pegmatites are tantalum rich (Ginzburg, 1972). The high content of Mn and Ti corroborate the presence of mangano-ilmenite minerals.

6. Discussion

The geochemical data of granitoids of studied area were plotted on Ternary diagram which falls in the bearing of tin field (Fig. 3; Singh and Singh 2011). There is no definite relationship observed among the variation of tin with other major oxides. Several lines of field, petrographic analysis and bulk geochemistry of KG, KGG and pegmatites (KP) reveal that stanniferous peraluminous KG and KGG granitic melt originated from the crustal anatexis i.e. partial melting of crustal source.
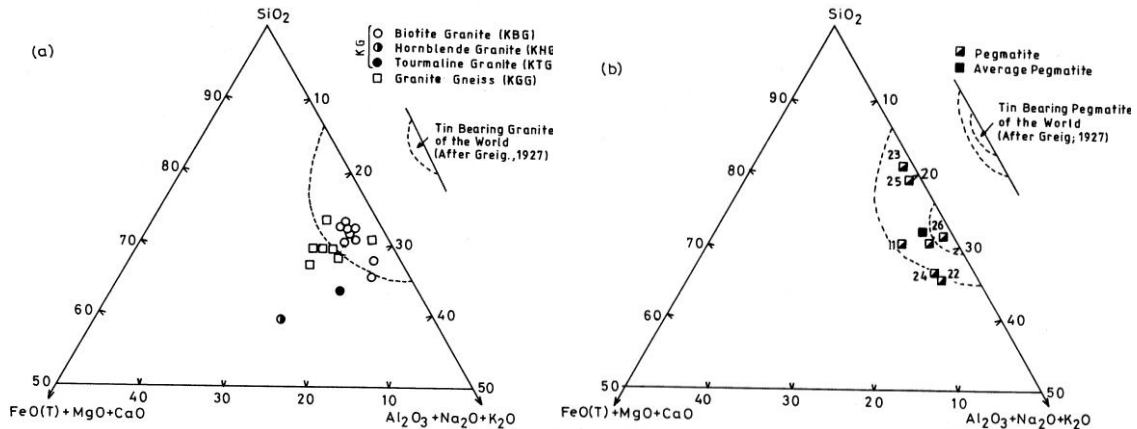

Fig. 3: Ternary diagram SiO_2-$(FeO^* + MgO + CaO)$ - $(Al_2O_3 + Na_2O + K_2O)$ of the tin bearing granitoids (a) and pegmatites (b) of the Katekalyan area, district Dantewada, Chhattisgarh (Stemprok and Sulcek, 1969).

The microclinisation process show the enrichment of K_2O at the expense of Na_2O and change in petrochemical composition, where plagioclase is replaced by the microcline in the granitic rocks. Albitisation seems more frequent than microclinisation and may be accompanied by lithium enrichment.

The partial melting model given in figure 4 and this shows that the variation of KG as well as KGG can be explained by varying degree of partial melting (5 to 50%) of bulk continental crust but distribution coefficient for Sr (d_{Sr}) must be very low i.e. <<10. The anorthite content of feldspar is very sensitive to determine the distribution coefficient of Sr, therefore, a small changing D_{Sr} will shift the vertical trend of partial melting of source towards higher or lower sides of Sr content. The result of partial melting modeling at least suggests that the differentiation of KG and KGG melt are more governed by partial melting of bulk crust rather than fractional crystallization. The estimates upper limit of partial melting i.e., 50 % of bulk crust noted for KG and KGG are consistent with required rheological, critical melt percentage to leave the source region has decreased granite melt which were capable to mineralised tin ore elements.
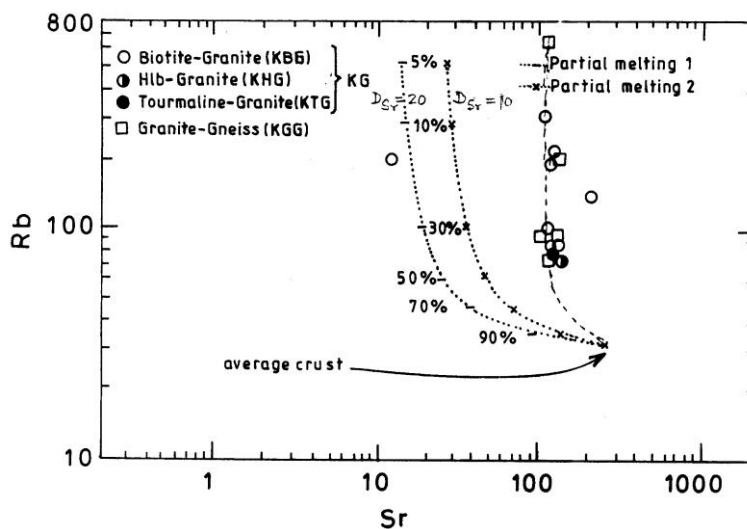
Fig. 4: Partial melting models (1 and 2) of bulk crust composition (Sr = 260 ppm, Rb = 32 ppm) of Taylor and Mc Lennan (1985) calculated at D_{Sr} = 20 and D_{Sr} = 10 respectively as shown by Gasparon et al. (1993) and compared with the variation of KG and KGG, approximately by 5-50% melting of average crust silicate. D_{Sr}<<10. See text for discussion.

Winchester and Max (1983) have used the trace element parameters viz., Rb/Sr vs Sn (Fig. 5a) and TiO2 vs Sn (Fig. 5b) as originally proposed by Lehman (1982), which discriminate Sn-rich and Sn-poor compositional trends from the Greenville granite gneiss. The granite (KG) and granite gneiss (KGG) both follow Sn-enriched trend (Fig. 5). This feature of tin enrichment trend may probably indicate that generation of KG melt by melting of KGG protolith and further enriched in the late stage fractionation of KG, because the later is relatively richer in tin content compared to the former one.
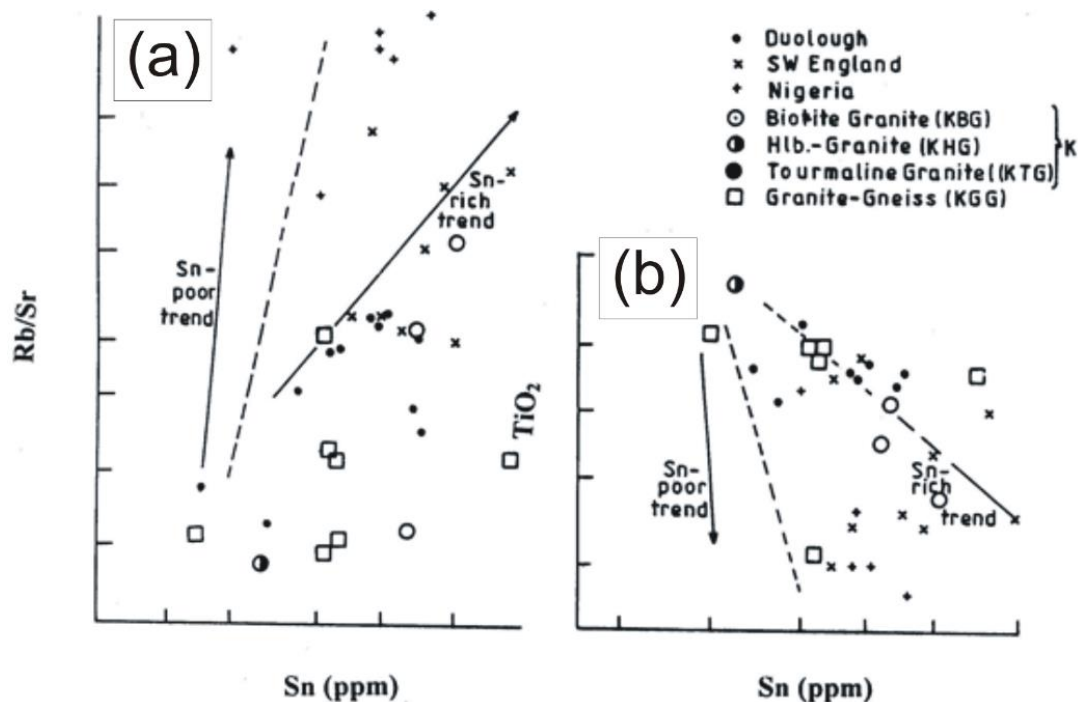

Fig. 5: Rb/Sr Vs Sn (a) and TiO_2 Vs Sn (b) variation diagrams (after Lehmann, 1982; Winchester and Max, 1983) contrasting Sn-rich and Sn-poor trends. Note that KG (KBG and KHG) and KGG mostly coincides with Sn–rich trends. The broken line separates the Sn-poor and Sn-rich fields.

7. Conclusions

The tin (Sn) content in KBG (av. 76.55 ppm) is found more than the saturation level of 50 ppm, comparison to KGG (av. 16.14 ppm) might be due to the effect of post-magmatic and late metasomatic processes. The partial melting modeling at least suggests that the differentiation of KG and KGG melt is more governed by partial melting of bulk crust rather than fractional crystallization. The association of cassiterite, lithium mica (lepidolite) and fluorite in the pegmatites may be possible that the tin transported in the gaseous stage as SnF_4 or $SnCl_4$. The apical zones of tin-bearing granitoids are sites of intense and more complex metasomatic activity with the transportation of tin ions leading to the formation of discrete crystals of cassiterite.

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