ORE PETROGRAPHY, ALTERATION AND GEOCHEMISTRY

5.1. Ore petrography

5.1.1. Introduction

Ore petrography is done best on a very well polished ore section. But for achieving a perfectly polished ore section there are always difficulties mainly due to variation in mineral and ore composition as well as their hardness. The present study is also no exception to it; however, the author has adopted the following procedure for the opaque sections.

First a suitable sized ore samples were selected 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 usual precautionary measures were strictly followed during the final polishing. Special care was taken in case of such samples which appeared altered or having mineral constituents of variable hardness. In such cases, alumina or diamond polishing was done very slowly but with uniform light pressure.

5.1.2. 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.). The standard work of Ramdohr (1969), Schouten (1962) and Utenbogaardt and Burke (1971) were consulted.
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 of the Katekalyan have been studied in detail and is divided into two main classes, namely primary and secondary ore minerals with the salient features are given below.

(A) Primary ore minerals

Cassiterite (SnO₂, Tetragonal):

Cassiterite is most important ore mineral of the study area. The major bulk of this ore mineral is associated with pegmatites. It occurs mainly as coarse disseminated grains ore body with euhedral to subhedral shape and bipyramidal form and massive in nature. The mineral is dark gray to black in colour with grayish to brown streak and greasy to adamantine lustre.

Cassiterite is brownish grey to light grey in colour and have pitted (poor polishing) to non-pitted surface in reflected light. The intensity of the colour was lower than that of associated columbite-tantalite. The reflection pleochroism is very weak and varies from brownish grey to orange red. The internal reflection colour (Plate XXIII, Fig.A) shows distinct anisotropism from light grey to dark grey and a brick red to yellow pale brown. The orange red pleochroic colour and the brick red internal reflection may be 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). Anisotropy and strong internal reflection and high
relief are also additional distinguishing characters for the identification of the cassiterite mineral. In many polished sections of cassiterite two sets of very feeble cleavage traces have been observed only under cross-nics (Plate XXIII, Fig. A). Ore microscopic studies on the cassiterite samples of the study area reveal the presence of numerous inclusions (or exsolutions) of minerals. These inclusions were observed to contain columbite-tantalite, tapiolite and silicate minerals. Exsolution texture among cassiterite, columbite-tantalite and tapiolite is a common phenomenon and helpful in the understanding the genesis of mineralisation.

The coarse grains of cassiterite are usually fractured which are filled by the quartz and columbite-tantalite minerals (Plate XXIV, Fig. A and B). Cassiterite often occurs with tapiolite where later has no internal reflection. However, their intergrowth is subjected to alteration particularly at the contact. The altered phase shows white internal reflection of microlite whereas tapiolite shows reddish internal reflection (Plate-XXIII, Fig. A).

Few cassiterite samples exhibit zoning from colourless to brown shades (Plate XXIII, Fig. A) 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.

**Columbite-tantalite** $\{(\text{Fe,Mn}) (\text{Ta,Nb})_2\text{O}_8, \text{Orthorhombic}\}$:

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 (Plate XXIII, Fig. D) are irregular in shape and vary in size from small globules to large lamellar grains (Plate - XXV, Fig. B). Babu (1994) suggested that columbite-tantalite is the solid
solution series between columbite (FeMn)Nb₂O₆ and tantalite (Fe,Mn)Ta₂O₆ and is commonly associated with cassiterite in Kataklyan.

The ore petrography suggests that some of the larger grains of columbite-tantalite are definitely the product of normal intergrowth. The columbite-tantalite minerals are easily identifiable by their moderate reflectivity (whitish grey) than that of cassiterite, and weak but distinct pleochroism. Columbite/tantalite shows very weak anisotropism and straight extinction. In the coarse crystals of columbite-tantalite veinlets of cassiterite have been observed along fractures. Where subhedral cassiterite grains were found to have columbite-tantalite inclusions with the development of radiating cracks. Occasionally columbite-tantalite also occur as fracture fillings in cassiterite (Plate -XXV, Fig. A). The textural study suggest that columbite-tantalite appears replacing cassiterite and vice-versa texture frequently. But columbite-tantalite shows very rare (or some what unusual) inclusions of wolframite and tapiolite.

**Tapiolite [(Fe,Mn) (Ta,Nb)₂O₆ – Tetragonal]:**

The tapiolite mineral is also present a very miner constituent cassiterite association. It occurrence as separate phase is expected in the area, but due to similarity in physical properties with other associated ore minerals makes it difficult to distinguish it individually in the field. Tapiolite mostly occurs as very small grains, bluish grey in colour with brownish tint (Plate -XXIV, Fig. D).

In reflected light, its reflectivity is low and it looks bluish grey. Thus it is of slightly higher reflection colour than that of cassiterite. 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 (Plate -XXIII, Fig. C). It is easily distinguished from cassiterite by its slightly higher reflectivity, better polishing, lower micro-hardness and moderate anisotropism. It is distinguished by its higher anisotropism, low internal reflection and better polish (Plate XXIII, Fig.B) from columbite-
tantalite. In general, the paragenetic relation of this mineral with the other associated ores indicates that it has intergrowth with cassiterite or as replacement type texture with the original tin mineral but very rare textural relationship with columbite-tantalite mineral.

**Microlite** [(CaNa)₂(Ta₂O₆) (O, OH, F) – Isometric]:

The microlites mostly occur peripheral to the columbite-tantalite and might be secondary product of the latter (Plate XXV, Fig. C).

**Wolframite** [(Fe,Mn)WO₄ – Monoclinic]:

It is observed as an inclusions in cassiterite, columbite-tantalite and very rarely in tapiolite. Its reflectivity is moderate and similar to that of columbite-tantalite. The tungsten mineral may be distinguish from columbite-tantalite by the difference in the shades, that is, the tungsten mineral is more grayish white than the whitish gray of columbite-tantalite (Plate XXIII, Fig.D). Moreover, it is having much deeper red internal reflection. Sometimes the bladed form having slanting terminations is helpful in distinguishing wolframite from similar looking opaques.

It is also distinguished from cassiterite by higher reflectivity, better polishing and strong anisotropyism. Reflection pleochroism in wolframite is quite low and can be seen along grain boundaries. The textural study points the presence of tiny inclusions, which suggest that wolframite should be related with early paragenetic sequence than cassiterite (Plate XXV, Fig.D).

**Secondary minerals**

Goethite, in many samples of cassiterite intergrowth with other cassiterite bearing minerals like columbite-tantalite and tapiolite. The fine veins and veinlets of goethite (Plate XXIII, Fig.B), were noticed randomly with tin ore. The goethite is present with grayish reflection colour in reflected light. Sometimes varying between dull gray to bright gray with a bluish tint.
Occasionally it reflects the dull gray reflection, which suggest that the iron hydroxide is not fully crystalline.

5.2. Alteration environment

The formation of cassiterite mineral in the study area is mainly associated with the metasomatic replacement of granitic rocks. The granites are recrystallised by hot gaseous, aqueous mineralised solutions will continue to exchange and receive elements from the wall rocks by the several differing alteration effects may occur at different points. The pneumatolytic alteration in the rocks is due to the combined effects of heat and magmatic emanations largely consisting of the halogen elements, water phosphorus and alkali metals.

Different alteration zones associated with tin mineralisations have been identified in the study area based on field evidences and petrographic and geochemical studies of the granitoids. The influence of different zones with the changes of mineralogical and petrochemical variants shows different alteration activity.

The different metasomatic activities leads to the formation of rare metal mineralisation have been recognised in the study area. Four distinct zones of formation of cassiterite along with Nb and Ta mineral compositions have been demarcated viz, microclinisation (potash-metasomatism), albitisation (soda-metasomatism), greisenisation (pneumatolytic activity) and sericitisation in the Katekalyan granites and pegmatites.

It is commonly observed that tin deposits are mainly confined at the contact of metasediments, metabasics & granites/granite gneisses with pegmatites and quartz veins in Katekalyan. The alteration zones in this area are very narrow. The apical zones of tin-bearing granitoids are sites of intense
and complex metasomatic activity with the transporation of tin ions leading to the formation of discrete crystals of cassiterite. Source of the alteration solutions is highly debated. Feldspathisation takes the form of microclinisation or albitisation. The enrichment of K₂O at the expense of Na₂O and change in petrochemical composition indicate by the process of microclinisation, where plagioclase is replaced by the microcline in the granitic rocks. Albitised pegmatites in Katekalyan area were found in granites and metabasic rocks. 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. Albitisation seems more frequent than microclinisation and may be accompanied by lithium enrichment. Albite enrichment of this type is difficult to recognise particularly where the rocks are only partially altered. The phenomenon of albite enrichment is accompanied by the presence of disseminated cassiterite rich with minor or rare 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. Geochemically, the import of OH, F, Li, Sn, W, B and the removal alkalis (especially Na, less pronounced K) are the most significant, while Si, Al remain 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 opaques minerals. It has been commonly observed that in Katekalyan area, mineralisation is associated with wall rock alteration and also the intensity of alteration is directly proportional to the intensity of mineralisation.

5.3. Geochemistry of Cassiterite

To study the main ore minerals found in the pegmatites as cassiterite along with columbite and tantalite in varying proportions, eight representative samples of cassiterite have been analysed. Ore samples were selected from six important mineralised pegmatites. Three samples were taken from placer deposits of the different localities.

5.3.1. Samples preparation method

First, cassiterite grains were separated manually from rich clots of ores. Then each samples were washed in water carefully, dried and crushed. Further, samples were powdered in agate mortar and sieved to different fractions. To get finer fragments free from dust, the sieved material was washed in water again and dried. After this the samples were treated with dilute HCl to make it free limonitic impurities and washed again with pure water and dried. The samples were passed through isodynamic separator to get pure concentrates of ores. Finally, the ore concentrates were checked under binocular microscope to remove the composite grains and extraneous mineral particles.

5.3.2. Procedure of XRF analysis

5 to 6 gms – 100 mesh sample is mixed with 1 ml 5% polyvinyl acetate in acetone. The mass is pressed into pellet of 40 mm diameter at 30-kilo newton pressure. The same pellets were analysed for the elements of Sn, Nb, Ta, WO₃ and others using XRF instruments (Philips Make Model PW-1400).

The analytical data are given in table 5.1.
Table 5.1. Element Analyses of Cassiterite from Katekalyan Area

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>R89/517</th>
<th>R89/612</th>
<th>R89/790</th>
<th>R89/830</th>
<th>R89/915</th>
<th>R89/1305</th>
<th>R89/1399</th>
<th>R89/1405</th>
<th>Average</th>
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<tr>
<td>Ref./Spot No.</td>
<td>CF/1210</td>
<td>CF/1220</td>
<td>CF/1230</td>
<td>CF/1240</td>
<td>CF/1250</td>
<td>CP/5</td>
<td>CP/99</td>
<td>CP/105</td>
<td></td>
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<tr>
<td>Sn (%)</td>
<td>56.57</td>
<td>61.98</td>
<td>60.12</td>
<td>71.84</td>
<td>70.76</td>
<td>63.68</td>
<td>69.78</td>
<td>62.34</td>
<td>64.63</td>
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<tr>
<td>Nb (%)</td>
<td>0.97</td>
<td>0.52</td>
<td>0.89</td>
<td>0.76</td>
<td>0.96</td>
<td>0.79</td>
<td>0.84</td>
<td>0.75</td>
<td>0.81</td>
</tr>
<tr>
<td>Ta (%)</td>
<td>2.11</td>
<td>2.29</td>
<td>2.18</td>
<td>1.99</td>
<td>1.87</td>
<td>2.16</td>
<td>2.05</td>
<td>1.89</td>
<td>2.07</td>
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<tr>
<td>WO₃ (%)</td>
<td>2.54</td>
<td>2.48</td>
<td>1.83</td>
<td>2.38</td>
<td>2.46</td>
<td>1.95</td>
<td>2.58</td>
<td>2.19</td>
<td>2.30</td>
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<td>FeO₇ (%)</td>
<td>11.58</td>
<td>11.49</td>
<td>10.99</td>
<td>11.38</td>
<td>11.27</td>
<td>NA</td>
<td>0.01</td>
<td>0.13</td>
<td>8.12</td>
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<td>MnO (%)</td>
<td>7.22</td>
<td>5.86</td>
<td>6.78</td>
<td>7.17</td>
<td>6.66</td>
<td>2.16</td>
<td>2.09</td>
<td>2.38</td>
<td>5.06</td>
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<tr>
<td>MgO (%)</td>
<td>2.13</td>
<td>2.34</td>
<td>2.09</td>
<td>1.99</td>
<td>2.19</td>
<td>3.79</td>
<td>3.69</td>
<td>3.56</td>
<td>2.72</td>
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<tr>
<td>TiO₂ (%)</td>
<td>0.11</td>
<td>0.09</td>
<td>0.14</td>
<td>0.18</td>
<td>0.07</td>
<td>0.45</td>
<td>0.39</td>
<td>0.41</td>
<td>0.23</td>
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<tr>
<td>CaO (%)</td>
<td>1.39</td>
<td>1.28</td>
<td>1.43</td>
<td>1.32</td>
<td>1.16</td>
<td>3.98</td>
<td>3.76</td>
<td>3.57</td>
<td>2.24</td>
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<td>Ni (ppm)</td>
<td>16.00</td>
<td>14.00</td>
<td>18.00</td>
<td>13.00</td>
<td>17.00</td>
<td>16.00</td>
<td>15.00</td>
<td>17.00</td>
<td>15.75</td>
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<td>Ga (ppm)</td>
<td>42.00</td>
<td>40.00</td>
<td>43.00</td>
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<td>94.00</td>
<td>89.00</td>
<td>95.00</td>
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</tr>
<tr>
<td>Rb (ppm)</td>
<td>53.00</td>
<td>51.00</td>
<td>51.00</td>
<td>54.00</td>
<td>49.00</td>
<td>52.00</td>
<td>51.00</td>
<td>48.00</td>
<td>51.12</td>
</tr>
</tbody>
</table>

5.3.3. Chemistry of Cassiterite

The element analyses of cassiterite given in Table 5.1 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 SnO₂ 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 other major oxides present are WO₃ 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%; TiO₂ 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.

Niobium (Nb) and tantalum (Ta) are characteristically oxyphilic forming a number of complex minerals or they enter isomorphously into minerals of iron, manganese, titanium, tin, tungsten, uranium, thorium and rare earths. Niobium (Nb) shows closer relationship with titanium, tungsten, thorium, the rare earths of cerium group and sodium. Tantalum (Ta) shows a closer relationship 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 are indicative of the presence of mangano-ilmenite. The average Sn content in cassiterite samples from the study area is 64.63%, which is considered to be of economically importance. Almost all the cassiterite samples contain significant amounts of Sn, Nb, Ta and W. Whether these elements are present in sufficient quantities to render profitable extraction from these cassiterite crystals.
PLATE – XXIII

Fig (A): Photomicrograph of cassiterite 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 x 0.32 x 4) [Crossed]

Fig (B): Photomicrograph of cassiterite (dark) is showing intergrowth with tapiolite (bright) present as twin lamellae. On the sides of this intergrowth, columbite-tantalite (yellowish cream) appears to replace it and also show the presence of goethite.

(Reflected Light, 10 x 7) [Uncrossed]

Fig (C): Photomicrograph showing the intergrowth of cassiterite and tapiolite (typical colour) with development of criss-cross fractures traversing the body of the crystal. This tapiolite shows strong anisotropism but it is masked its internal reflection.

(Reflected Light, 10 x 7) [Uncrossed]

Fig (D): Photomicrograph showing the intergrowth of pitted cassiterite and columbite-tantalite (whitish gray). The wolframite (grayish white) is present at the contact of cassiterite.

(Reflected Light, 10 x 7) [Uncrossed]
PLATE – XXIV

Fig (A): Photomicrograph of cassiterite crystal (dark brown) shows the intergrowth of columbite-tantalite with varying shape.

(Reflected Light, 10 × 7)
[Uncrossed]

Fig (B): Same photomicrograph of Fig. (A), in which 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]

Fig (C): Photomicrograph shows the development of cassiterite (light) by the alteration of the lithium bearing mica (brown) within the mass of cassiterite.

(Reflected Light, 10 × 7)
[Uncrossed]

Fig (D): Photomicrograph shows the 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]
Fig (A): Photomicrograph of coarse-grained cassiterite (light gray) having triangular Pิตs with zoned surfaces of colourless to brown shades are present.

(Reflected Light, 10 x 7)
[Uncrossed]

Fig (B): Photomicrograph of coarse cassiterite (brownish) with exsolved grains of columbite-tantalite (whitish gray) having alternate irregular in shape and varying in size from globules to large lamellar grains. Microlite is also present having the white internal reflection.

(Reflected Light, 10 x 7)
[Uncrossed]

Fig (C): Photomicrograph of 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 x 7)
[Uncrossed]

Fig (D): Photomicrograph of coarse-grained cassiterite (brown) shows the inclusions of columbite-tantalite (whitish gray) and wolframite (grayish white).

(Reflected Light, 10 x 7)
[Uncrossed]