CHAPTER 1

INTRODUCTION
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Molybdenum (Mo) was discovered by Swedish chemist Carl William Scheele in 1778, and was named after the Greek word *molybdos*, which means *lead*. But, the metal has been in usage only since 19th century. Its main sphere of applications (80-95%) is as an alloy with Fe, V, W, Cu, Ni, and Co as well as with carbide. Molybdenum deposits are generally associated with acid igneous rocks of intrusive character generated in a continental environment (Mutschler et al, 1981; Westra and Keith 1981). The crustal average is reported to be 1-2 ppm (Kuroda and Sandal, 1954; Taylor, 1964; Mason and Moore 1982).

The largest use of molybdenum (Some times called moly for short) is as an alloy in the manufacture of stainless steels and alloy steels particularly for high strength and corrosion-resistant requirements viz., water distribution systems, food handling equipment, chemical processing equipment, home, hospital, and laboratory equipments etc. Alloy steels include the stronger and tougher steels needed to make automobile parts like bearings, machine components, construction equipment, gas transmission pipes, mill rolls, crusher parts; super alloys for use in furnace parts, gas turbines etc. Molybdenum is also an important material for the chemicals and lubricant industries. Moly has uses as catalysts, paint pigments, corrosion inhibitors, smoke and flame retardants, dry lubricant (molybdenum disulfide) on space vehicles. Molybdenum can also be used in the production of rechargeable dry batteries; these lithium-molybdenum batteries have more power per cell volume than conventional nickel-cadmium or alkaline batteries. As a pure metal, molybdenum is used because of its high melting temperatures as filament supports in light bulbs and furnace parts. Molybdenum is one of an essential element in plants and animals, in plants; for example, the presence of molybdenum allows the plant to absorb nitrogen. It is used as a catalyst in crude oil refineries to removes sulphur. The overall general uses for molybdenum are in
machinery (35%), for electrical applications (15%), in transportation (15%), in chemicals (10%), in the oil and gas industry (10%), and assorted others (15%).

The most important ore source of molybdenum is the mineral molybdenite (MoS₂). A minor amount is recovered from the mineral wulfenite. Some molybdenum is also recovered as a by-product or co-product from copper processing/production. (Mutschler et al. 1981; Westra and Keith 1981).

1.1 World Occurrence of Molybdenite

Three fourth of the world reserves of molybdenum are in the western cordilleran areas of North and South America. The remaining one forth of the World’s reserves occur in the porphyry deposits now being developed in locales extending from the Philippines to New Guinea, Russia, Europe, China, and in Australia.

Distribution of molybdenum reserves and productive capacity is concentrated only in few countries of the world. World mine output is estimated to be 135,000 metric tons (molybdenum contained in concentrate), of which, United States, China, Chile, Canada, and Mexico provided more than 91%. These five countries are expected to continue as the principal producers as they possess about 90% of the estimated 12 million tons of molybdenum in the world reserve base. The world reserve base is 19 million tonnes mainly located in North America, Chile, Mexico, China and the countries from the former Soviet Union. (Table 1).

1.2 Production and Consumption

The annual production and consumption of molybdenum are a little over 300 million pounds of molybdenum. The detailed consumption and production statistics is given in the Figs 1.1 and Fig 1.2. Apart from U.S, China, Chile Canada and Other countries include Mexico, Peru, Iran, and former Soviet Union (Mineral Commodity Summaries, January 2004). It is clear from the figure that most of Molybdenum production comes from USA and Western European countries consume significant portion of Molybdenum.
Table 1: World mine production Reserves and Reserve base (U.S. Geological Survey, Mineral Commodity Summaries, Jan 2004)

<table>
<thead>
<tr>
<th></th>
<th>MINE PRODUCTION</th>
<th>RESERVES</th>
<th>RESERVE BASE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2002</td>
<td>2003</td>
<td>In 000' metric tonnes</td>
</tr>
<tr>
<td>United states</td>
<td>32,600</td>
<td>34,100</td>
<td>2,700</td>
</tr>
<tr>
<td>Armenia</td>
<td>3,500</td>
<td>4,000</td>
<td>200</td>
</tr>
<tr>
<td>Canada</td>
<td>7,500</td>
<td>7,500</td>
<td>450</td>
</tr>
<tr>
<td>Chile</td>
<td>29,500</td>
<td>31,400</td>
<td>1,100</td>
</tr>
<tr>
<td>China</td>
<td>29,300</td>
<td>30,000</td>
<td>3,300</td>
</tr>
<tr>
<td>Iran</td>
<td>1,700</td>
<td>1,700</td>
<td>50</td>
</tr>
<tr>
<td>Kazakhstan</td>
<td>230</td>
<td>225</td>
<td>130</td>
</tr>
<tr>
<td>Kyrgyzstan</td>
<td>250</td>
<td>250</td>
<td>100</td>
</tr>
<tr>
<td>Mexico</td>
<td>3,400</td>
<td>3,500</td>
<td>90</td>
</tr>
<tr>
<td>Mongolia</td>
<td>1,590</td>
<td>1,500</td>
<td>30</td>
</tr>
<tr>
<td>Peru</td>
<td>9,500</td>
<td>9,500</td>
<td>140</td>
</tr>
<tr>
<td>Russia</td>
<td>2,900</td>
<td>2,900</td>
<td>240</td>
</tr>
<tr>
<td>Uzbekistan</td>
<td>500</td>
<td>500</td>
<td>60</td>
</tr>
<tr>
<td>World Total</td>
<td>122,470</td>
<td>127,075</td>
<td>8,600</td>
</tr>
</tbody>
</table>

Fig. 1.1: Molybdenum Production by geographic regions (1999-2002).

Fig. 1.2: Molybdenum Consumption by Geographical Region (1999-2002)
1.3 Indian Resources

In India, the molybdenum is generally associated with base metal sulphide ores. Rakha copper deposit in Jharkhand contains 45 to 48 ppm of molybdenum and Malanjkhand copper deposit of Madhya Pradesh contains 0.04% recoverable molybdenum. Dariba-Rajipura lead zinc deposit of Rajasthan contains molybdenum besides bismuth, arsenic and cadmium. The multimetal deposit at Umpyrtha in Khasi and Jaintia hills of northeastern India contains copper, lead, zinc, and molybdenum. Molybdenum deposit in Karadikuttam in Madurai district, Tamil Nadu contains 0.02 to 0.14% recoverable molybdenum. The reserves of the country are given in the Table 2 below.

Table 2: Reserves of Molybdenum ore (by State and grades) Source: IBM Mineral year Book 2000

<table>
<thead>
<tr>
<th>State / Grade</th>
<th>Proved</th>
<th>Probable</th>
<th>Possible</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>All India</td>
<td></td>
<td>3600</td>
<td>80,009,00</td>
<td>80,369,00</td>
</tr>
<tr>
<td>Ore Contained MoS₂</td>
<td>--</td>
<td>62</td>
<td>2764</td>
<td>2826</td>
</tr>
<tr>
<td>Karnataka</td>
<td>--</td>
<td>900</td>
<td></td>
<td>900</td>
</tr>
<tr>
<td>Ore Contained MoS₂</td>
<td>--</td>
<td></td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Madhya Pradesh</td>
<td></td>
<td></td>
<td>80,000,00</td>
<td>80,000,00</td>
</tr>
<tr>
<td>Ore Contained MoS₂</td>
<td>--</td>
<td></td>
<td>2762</td>
<td>2762</td>
</tr>
<tr>
<td>Tamil Nadu</td>
<td></td>
<td>3600</td>
<td></td>
<td>3600</td>
</tr>
<tr>
<td>Ore Contained MoS₂</td>
<td>--</td>
<td>62</td>
<td></td>
<td>62</td>
</tr>
</tbody>
</table>

1.4 Review of Molybdenite association

One forth of the world’s molybdenum productions is derived from porphyry copper deposits. The porphyry deposits have an average MoS₂ content varying from 0.1 to 0.5 percent.
The types of commercial deposits are:

1. Porphyry or Disseminated ore including Stockworks and Breccia pipes: Climax, Urad-Henderson, Questa, Bingham and numerous porphyry copper deposits.

2. Contact Metasomatic; Pine Creek, California, Helvetia, Arizona, Kanben, Norway, north eastern Caucasus, Russia, China, Azegour and Morocco.

3. Quartz vein; Questa, New Mexico.

4. Pegmatite and Applite dykes; most mine Quebec, Valdor and Preissac, Quebec.

5. Banded deposits in sedimentary rocks; Arizona, Utah, Colorado, New Mexico, Wyoming, South Dakota and Texas.

1.5 Literature Review

Krishnamurthy et al (1987) have carried out a detailed and comprehensive geological mapping of Granite-greenstone belts of Raichur district.

Rao (1987) has reported molybdenite mineralization associated with granites from Maltgud area of Raichur district.

Rao and Vidyadharan (1989) have indicated the transitional I and S types granites implying middle to lower crustal source for the Mo mineralization of Malatgud area.

Chandrashekaraiyah (1992) has reported Mo in litho geochemical samples of Raichur district.

Prakash (1996) has reported the occurrence of Molybdenite mineralization ranging from 15 ppm to 3.26% in granites in and around Ashapura area along with, Tungsten, copper and silver. The mineralization is noticed in leucogranitic dyke and in pink granites.
Chandrashekaraiah and Janardhana Rao (2001) while carrying out the regional geochemical survey in Raichur and Siwar areas have revealed significant values of Bismuth, Tungsten and Molybdenum in granite-greenstone terrain of Raichur district.

Omkesha Murthy et al (2004) have carried out the fluid inclusion studies and have concluded that the Molybdenite mineralization at Ashapura area took place at temperatures of >370 °C and 2.5-3.0 kb pressure.

1.6 Scope of the Thesis

Molybdenum is a strategic metal. Though there are very few known small molybdenite occurrences in India, none of the occurrence is mined in spite of the fact that the molybdenum forms a very important alloy of steel. Most of the molybdenite deposits are associated with granitic rocks. Recently, Geological Survey of India has located number of molybdenite deposits in south India. Except the reports on occurrences there is no detailed work on the geochemistry and genesis granite molybdenite association. Therefore, in the present study an attempt is being made to study in detailed the Mo occurrence in Ashapura area of Raichur district. The geochemical characteristics of the associated granitic rocks and the role of the ore forming fluids are the main interest of this study.

1.7 Objectives

1. Preparation of a geological map of the study area including lithologies that host Mo mineralization.

2. Detailed field study and mapping of the mineralised zone.

3. Generation of Petrographic, mineralogical and geochemical database for the study area.

4. To determine the nature and composition of the ore fluids that are responsible for the Mo concentration.
1.8 Methodology

1.8.1 Field Study and Geological Mapping

Mapping and collection of samples was carried during the field study. Mapping was done initially on 1:25,000 scale using the Survey of India topographic sheets and available published map. During field study efforts were put in to collect representative samples from all the important field variations observed. There are few active stone quarries in the study area which provide ample opportunities to observe field relationships.

1.8.2 Petrographic Study

Thin and polished sections of the collected rock samples were examined under microscope to identify the minerals and textural features which eventually provided additional data in the identification of minerals and different lithounits.

Modal analysis was performed for representative thin sections using James Swift point counter. In order to have a reasonably good statistics, over 1,500 counts were done on each sample. Photo micrographs are taken using Motic Image Digital Camera.

1.8.3 XRF Analysis

The Major elements analysis of representative samples were carried out by X-ray fluorescence spectrometry (XRF), Philips PW 1400 smoothed d.c. X-ray generator which supplies to the X-ray spectrometry tube with an ultrastable high voltage and current up to 100KV, 80MA (maximum permissible load of 3000 W). The voltage adjustable from 10-100 KW in steps of 1KV and the stability of the current is from 4MA to 80MA. (The stability of current is better than 0.3% at main voltage variation of -15% to 10% the maximum drift of +1.7 and MA is 0.3% at temperature variation of 15°C the require water pressure is around 2 kg/cm² at a flow of 3.5 litres/min and the water chilling plant for recirculation is also furnished). Trace element analysis done by using AAS at GSI Bangalore.
1.8.4 Fluid Inclusion Study

Doubly polished plates were prepared for fluid inclusion studies. Depending upon the transparency of the rocks, the thickness of the wafers used ranged from 0.2 to 0.3 mm. Samples were prepared carefully, taking precaution to avoid both excessive heating and mechanical shattering.

Fluid inclusion observations were made using ordinary microscope. Microthermometric measurements were done using Linkham TH 600 dual purpose heating and freezing stage, with a facility to heat up to 600 °C and cool down to -196 °C by liquid nitrogen. Calibration was done using standard organic compounds. Precision in this study is estimated to be around +0.2 °C.

Heating and freezing studies were carried out adopting standard analytical procedure. The samples were preheated to +50 °C and then rapidly cooled. During reheating, various phases such as vapour, CO₂-clathrate (gas-hydrate), ice, salt hydrates and solid CO₂ formed in places of carbonic and aqueous liquids and heating was stopped upon complete homogenization of the fluid. Clathrate dissociation was determined with extreme care following temperature of recycling (Roedder, 1963) at the heating rate of 0.1-0.2 °C/min. Cooling was carried out at approximately at +0.5 °C/min.

The fluid inclusions study was carried out at the PPOD Laboratory, AMSE Wing, Geological Survey of India Bangalore. The temperatures have an uncertainty of +0.2 °C for below +30 °C whereas measurements around 250 °C are accurate to +1.5 °C. Salinities are expressed in wt.% NaCl equivalent determined from the equations of Potter and Brown (1977) and Potter et al. (1978.)

1.9 Location and Accessibility

Raichur district, which is situated in the northern part of Karnataka State, falls within the northern plane region of Karnataka State. The study area of Ashapura Molybdenite deposits is situated about 6 KM SSW of Raichur town lies between 16° 09’ and 16° 13’ North Latitudes and 75° 19’ and 77° 23’ East Longitudes. It is well connected by both road as well as rail. (Map 1)
1.10 Topography and Drainage

The topography of the area is a characteristic of granitic terrain, the rocks occur as a massive bouldery outcrop and at places as sheet rocks. The highest peak in the study area is 538M, which is 4 KM South East of the village Ashapura, there are other numerous hillocks around the study area. The drainage
is mostly dendritic type, which is the characteristic feature of granitic country rock. The streams and nalas have only a seasonal flow being completely dry in summer.

1.11 Climate, Rainfall and Vegetation

The area has a tropical climate. The major rainfall is from monsoon season only. Rainy season starts from July to September. The area remains dry in all other seasons. The temperature in the region ranges from 32 °C to 40 °C. The granite hills are barren, the vegetation is sparse except at few places where some shrubs and grass can be seen, some eucalyptus plantations are being made by the state forest department.

1.12 Regional Geology

The Dharwar Craton of southern India exposes a large section of Archaean continental crust and it is principally composed of low-K-tonalitic to trondhjemitic gneisses (Peninsular gneiss) with infolded Supracrustals (Sargurs) and capped by younger series metavolcanosedimentary sequences (Dharwars) and bounded late Archaean juvenile terrains in south. Calc-alkaline to K-rich granites form the latest Archaean magmatic event in the craton (Map 2). Recently Ramakrishnan (1994) divided green stone belts of Karnataka into Western and Eastern greenstone belts with respect to Closepet granite based on regional lithological variations, differences in volcano-sedimentary environments, magmatism and metamorphic grades. The strong N-S trending fabric of the Dharwar craton is partly due to the late Archaean transcurrent shearing episode (Drury and Holt, 1980; Chadwick et al., 1989) and is synchronous with the emplacement of Closepet granite (Jaynanda and Mahabaleswar, 1991). This belt of younger potassic granites is believed to make a major geo-suture joining two distinct crustal blocks of late Archaean age. Away from the main extent of this linearly disposed younger granites there are other isolated groups of younger granites like Chitradurga, Arsikere and Banavara in the west and Patna, Toranagal, Bellary and Raichur in the east.
The Western Dharwar craton (WDC) mainly comprises of Tonalite-Trondhjemite-Granodiorite (TTG) gneissic basement (Radhakrishna and Vasudev, 1977, Radhakrishna, 1983) overlain by greenstone belts. Whereas the Eastern Dharwar Craton (EDC) is made up of Late Archaean (2.6–2.5 Ga) granites intruding into older TTG gneisses (2.9–2.7 Ga) popularly known as Peninsular gneisses. Greenstones in the EDC are confined to small, elongated belts, which may represent terrain boundaries (Krogstad et al., 1989; Chadwick et al., 2000). Very recently Chadwick et al., 2000 have obtained the 3.3–2.7 Ga and 3.0–2.5 Ga ages for the WDC and EDC respectively.
MAP 1: Geological Map of Karnataka showing Ashapura area