

# Fluid Inclusion Characteristics of Tin-Tungsten and Copper Mineralisation in Tosham Igneous Complex of North Delhi Fold Belt, North Western India

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**Abstract** Tosham igneous complex occurs along northern part of the middle Proterozoic North Delhi fold Belt and metasediments of Delhi Supergroup. It comprises of Tosham porphyritic granite, rhyolite and quartz-porphyry. The Tosham granite and rhyolite hosts the tin-tungsten and copper mineralisation. Cassiterite and Wolframite occurs within the quartz veins and associated with other ore minerals such as chalcopyrite, pyrrhotite and pyrite. The foliation trend of the metasediments is N20 to 40°E parallel to the long axis of the hill. The mineralisation occurs near the granite-metasediments or granite-rhyolite contact in the western and eastern mineralised zones within Tosham hill. EPMA studies confirm the presence of cassiterite, pyrite, chalcopyrite, pyrrhotite, sphalerite etc. The fluid inclusions study reveals the existence of aqueous-gaseous (H<sub>2</sub>O-CO<sub>2</sub>+NaCl) fluid that underwent phase separation and gave rise to gaseous (CO<sub>2</sub>) inclusion. The carbonic inclusions show depression in Tmco (-65.2°C) due to the presence of CH<sub>4</sub> with CO<sub>2</sub> and also large no. of CH<sub>4</sub> inclusions are present and were confirmed by Raman spectroscopy and it was first time reporting in this area. The abundant of CH<sub>4</sub> inclusions over the CO<sub>2</sub> inclusions considered to be one of the diagnostic features of reduced porphyry copper type deposits. The salinity of tin/ tungsten mineralisation shows high to low (1.9 to 42.68wt % NaCl equivalents) and trapped at the estimate PT range from 2.1 to 3.5 kbar and 310 to 460°C. The eutectic temperature (Te) ranges from -50°C to -30°C reveals that the presence of chloride complexes such as FeCl<sub>2</sub>/MgCl<sub>2</sub> and CaCl<sub>2</sub> indicating the involvement of brines or complicated chloride mixtures in transporting Sn-W to the fluid system and evaluation of Sn-W ore fluids by high-salinity and high-temperature with the magmatic-hydrothermal activity either by immiscibility or mixing of fluids and evolution of granite/rhyolite induced the fluidisation and the presence of CH<sub>4</sub>/CO<sub>2</sub> influx might have triggered precipitation Sn-W and Cu mineralisation in the area.

**Keywords** Tosham, wolframite, tin, copper, granite, fluid inclusion

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## I. INTRODUCTION

The middle Proterozoic Delhi Fold Belt of western India hosts important base metal mineralisations in the entire stretch from southern part of Rajasthan to northern continuity in Haryana. In the northern part, mainly the Tosham area, comprised of Cu and Sn mineralisation. McMoham (1886) Ref. [1], first described the geology of the area and studied the petrography of felsites, quartz porphyry, granite and other rock types of this area and correlated the felsic volcanics and granites of Tosham with the Malani suite of igneous rocks of western Rajasthan. Kochhar (1983) Ref. [2] established a close association in space and time between the explosive felsic lava and high level nonorogenic subvolcanic granite which form distinct ring structure and also suggested that a hot spot related tectonics responsible for the igneous activity at Tosham. Rajashekharappa (1983) Ref. [3] gave petrographic studies and major elements data of all the rock types of the area and suggested the structure of Tosham igneous complex represents a caludron subsidence of a graben type.

Awasthi et al. (1977) Ref. [4] reported the occurrence of copper mineralization from this area and emphasised on the need for exploration for copper mineralization, whereas Dey (1978) Ref. [5] recorded the occurrence of copper minerals such as malachite, azurite, cuprite and chalcopyrite and concluded that copper mineralization is mainly restricted to western flanks of Tosham hillock. Geological Survey of India has carried out exploration for base metals involving geological mapping, geochemical sampling and drilling operations was carried out in and around Tosham area (Choudhary et al. 1984 and Kochhar et al, 1985) Ref. [6, 7]. Somani (2006) Ref. [8] studied fluid inclusions of hydrothermal solutions associated with Tin-Tungsten and copper mineralization at Tosham. Murao et al. (2008) Ref. [9] has carried out mineralogical evolution of Indium at Tosham in comparison with Goka area of Japan. Baniranjan Mishra and Subabhi Srivastava (2018) Ref. [10] carried out exploratory drilling in the

northern extension of Tosham hill for the understanding mineralisation in the northern extension of Tosham hill.

Fluid inclusions in transparent gangue minerals are thus commonly used to investigate metal precipitation conditions. This assumption is mainly based on the close spatial association of gangue and ore minerals (Campbell et al., 1984) Ref. [11]. In the last decade, new data sets have been published on the characterization of the fluid systems present during ore formation in different tin tungsten and polymetallic deposits worldwide, including advanced studies of Raman spectroscopy.

The present study deals with the geological setting of tin-tungsten and copper mineralisation hosted by granite/rhyolite in Tosham igneous complex. The petrographic and EPMA studies confirm that cassiterite occurs as disseminated and it is associated with pyrrhotite and chalcopyrite. The fluid inclusion studies of quartz veins reveals the evaluation of ore forming fluids for understanding of genesis and formation mechanism of Sn W-Cu mineralization associated with igneous complex of Tosham.

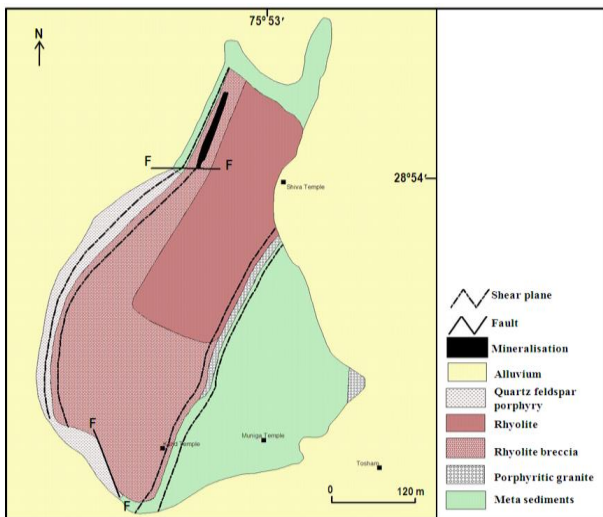


Figure 1. Geological map of the Tosham area (Modified after Kochar, 1983)



Figure 2a Field photographs of rhyolite



Figure 2b. Field photographs of porphyritic granite



Figure 2b. Field photographs of porphyritic granite



Figure 2d. Field photographs of meta sedimentary

## II. GENERAL GEOLOGY

The Tosham igneous complex comprises of granite porphyry and rhyolite are intruded in metasediments of Delhi Super Group of Proterozoic age and are equivalent to the Malani suite of rocks represented by the rhyolites and granites. The exposures of granite and rhyolite occur in isolated patches in a vast stretch of aeolian sands. The dome shaped Tosham hill forms a prominent topographic high above the plains. The three main suits of rocks were identified in the area are: quartz feldspar porphyry, central mass of rhyolites forming steep vertical cliff and also covered by rhyolite breccia, porphyritic granite and metasediments. The porphyritic granite intrudes metasediments and subsequently, both these formations have been intruded by hypabyssal rhyolite which forms the core/central part and surrounded by the rhyolite breccia of the Tosham hill. The foliation trend of the

metasediments is N20 to 40E parallel to the long axis of boundaries are sutured, interlocking with undulose the hill. Two prominent shear zones trending NNE and extinction. Iron oxide is seen as patches throughout the NNW with subvertical attitude, occur on the western and eastern faces of Tosham hill (Fig. 1). They are 10 to 15 wide and marked by close spaced open fractures with replacement of sulphides by iron oxides and malachite stains.

The Tosham area consists of granite and rhyolite rock is highly altered and the feldspar grains shows surrounded by sand and alluvium. Tosham igneous greenish colour and at places altered micaceous complex rocks of granite and rhyolite are related to minerals (Fig. 3b). The rhyolite rock is very fine grained, Erinpura Malani plutonic Neoproterozoic acid compact and massive. It is variegated colours of greenish magmatic event. The isolated hillocks of Tosham exposed grey, pinkish and brownish. The outcrop contains many are mainly of Post Delhi granitoids and consists of rhyolite joints filled with iron oxide and sulfides. The leaching of in the central part of the complex showing sharp contacts with rhyolite breccia and porphyritic granite. Urao et al. (2008) Ref. [09] suggested that the granites and rhyolites in the Tosham region formed 800 Ma, rhyolite effusion being slightly later than granite emplacement. This is also clearly borne out by the relationship between the two rock types seen in transverse sections across the Tosham hill is variegated from grey to yellowish grey to various shades of purplish brown (Fig. 2a). Flow banding is inward at high angles indicating magma viscosity high enough to prevent significant extrusion from the central part (Gupta and Rajashekharappa 1983) Ref. [12]. Rhyolite breccia occurs along the margins of the rhyolite and granite porphyry. The rhyolite breccia contains blocks of both accessory and accidental types of various rocks of volcanic matrix. Kochhar (1983) Ref. [2] has identified the rhyolite breccia on the basis of the subangular to angular and subrounded to rounded fragments of granite porphyry. The porphyritic granite exposed in the southern slope of the Tosham hill and the continuity of this rock type is concealed due to aeolocover (Fig. 2b). The Quartz feldspar porphyry dykes were observed in the field one is at SE side of the hill and another is NE side of the hill. This is clearly cutting across the rhyolite (Fig. 2c) and at contact chilled margins and size reduction is noticed. Meta sedimentary rocks of Delhi supergroup of rocks observed in the eastern side and NE of the Tosham hill it mainly consist of quartzite, micaceous quartzite, andalusite bearing quartzite and schists (Fig. 2d). The quartzite is dull white to light brown colour and medium grained and at many places, massive iron oxide staining observed. Two major shear zones on the western and eastern side of the rhyolite hills of Tosham are associated with mineralization. The surface indications like sulphide leaching, gossans, malachite stains and old working are the main evidence of mineralization. Tosham hill contains numerous joint sets filled with iron oxide minerals and at places fresh sulfide is also noticed.

### III. PETROGRAPHY

Meta sedimentary rocks of Delhi supergroup of rocks observed in the eastern side and NE of the Tosham hill. Metasedimentary rocks shows fine to medium grained quartz, muscovite, sericite, iron oxide and opaque minerals are common. Crude foliation planes define by micaceous minerals seen at places. Quartz grain

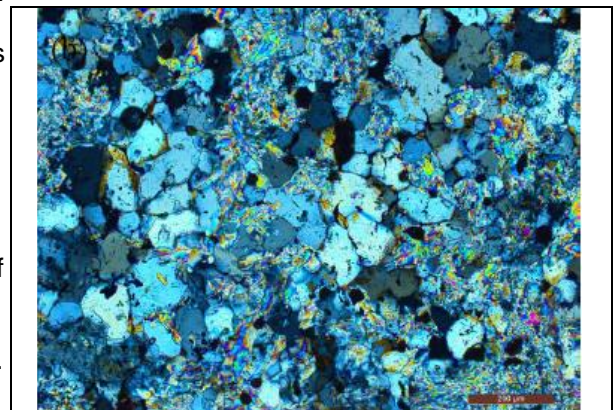


Figure 3a. Photomicrographs of metasedimentary rock

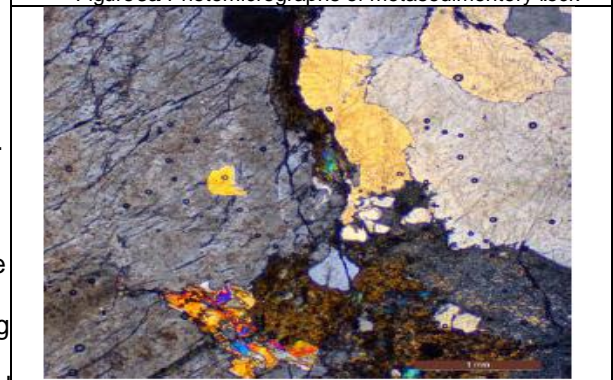


Figure 3b. Photomicrographs of porphyritic granite

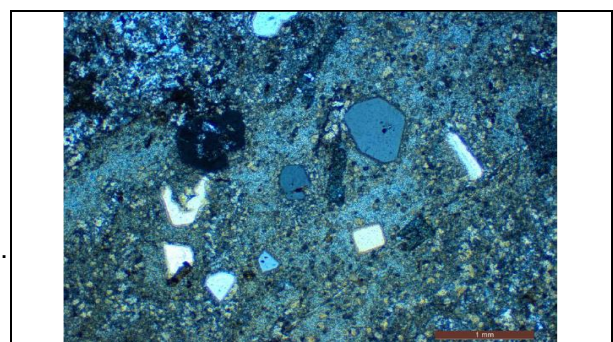


Figure 3c. Photomicrographs of rhyolite with porphyry clasts of quartz embedded in fine grained matrix

Ore microscopic studies were carried out on samples collected from surface and sub surface from Tosham area. The samples collected from the mineralized zone in the borehole drilled north of Tosham hill have studied (Fig. 3d & e). The major ore minerals observed under microscope are cassiterite, pyrrhotite, chalcopyrite and pyrite. Cassiterite usually seen associated with silicate minerals and sometimes seen associated with pyrrhotite and chalcopyrite and at fracture planes pyrrhotite and chalcopyrite is seen intruded into the grain boundaries of cassiterite (Fig3f). The pyrite is seen as fracture filled in later stage (Fig. 3g).



Figure 3d. Drill core of chalcopyrite mineralized zone



Figure 3e. sulphides seen as disseminations

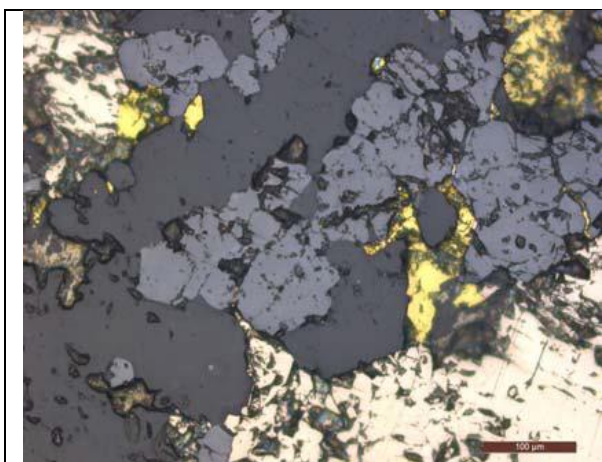


Figure 3f. Pyrrhotite and chalcopyrite seen intruded into the grain boundaries of cassiterite

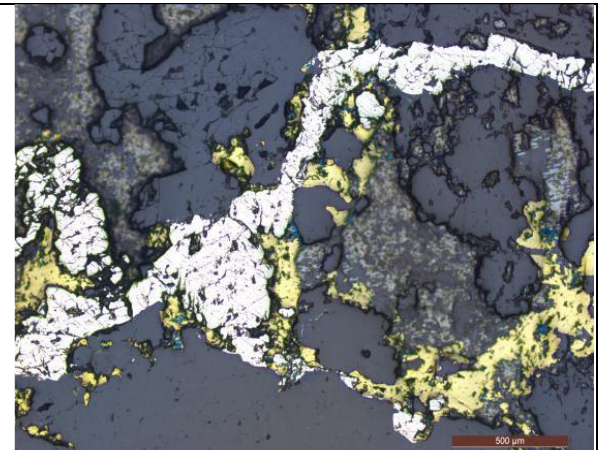


Figure 3g. Pyrite seen associated with chalcopyrite as a fracture filling.

#### IV. SN-W-CU MINERALISATION

Tosham igneous suite comprising of granite and rhyolite hosts the tungsten and copper and are associated with sulphide mineralisation localised mostly along the western and northern part of the Tosham igneous complex. An old working is located at west side at the contact of rhyolite and porphyritic granite. At western side of Tosham hill, malachite is seen associated with iron oxide veins and at places yellowish and red coloured gossans associated with iron oxides and at places hematite ore associated with quartz veins and even seen filled in joints and fractures. The main ore of (cassiterite) occurs as minute grains, specks, blades and disseminations in contact between meta sedimentary rock with porphyritic granite. The other associated ore minerals include wolframite, chalcopyrite, pyrite, stannite, pyrrhotite, cubanite, covellite etc. Cassiterite and Wolframite occurs intimately associated with quartz veins as fine 0.02 mm to coarse 1 cm grain and intergrowth with gangues as well as sulphides mainly chalcopyrite. It also occurs as exsolved belts within chalcopyrite. The Mineralization is observed from the relative variations in the contents of tin, tungsten and copper. The bulk of mineralisation occurs near the granite metasediments or granite rhyolite contact in the western and eastern mineralised zones within the Tosham hill. Copper mineralisation occurs in the forms of malachite and azurite stains, cuprite and chalcopyrite with pyrite, sphalerite along the contact zone of central rhyolite and western granite porphyry as fracture filling and disseminations, where as pyrite occurs as a thin stringers and veinlets and the tin mineralisation is associated with copper and tungsten. It averages 0.16% W, 0.53% Cu and 0.429% Sn and estimated 5.10 million tonnes (MECL). Based on detailed regional exploration of GSI, ore reserves of Sn, W and Cu have been estimated at 2.23 million tonnes up to a depth of 237 m below MSL with average grade of 0.28% Sn, 0.18% W and 0.24% Cu (Wokhoo and Prasad, 1989) Ref. [13].

## V. EPMA STUDIES

Chemical compositions of the polished thin sections were analyzed with the help of a four-wavelength dispersive spectrometer (WDS) attached to CAMECA SX10 electron microprobe analyzer at Center of Excellence in Geosciences Research (NCEGR), Geological Survey of India (GSI), Bangalore. Acceleration voltage of 15 kV and 20 nA beam current with a beam diameter of 1  $\mu\text{m}$ . The counting time was 10 and 5 s for the peaks and the background, respectively. Calibration processes were carried out separately for both silicate and sulfide minerals by using appropriate natural standards were chosen for calibration and ZAF corrections were made by the program PAP (Pouchou and Pichoir, 1984). [14]

The EPMA analysis of ore mineralised veins sample from Tosham area shows presence of cassiterite, pyrite, chalcopyrite, pyrrhotite, sphalerite etc. The main ore mineral of Cassiterite is associated with pyrrhotite and chalcopyrite (Fig. 3h). Cassiterite also occurs as disseminated and large grains having an inclusion of chalcopyrite (Fig. 3i).

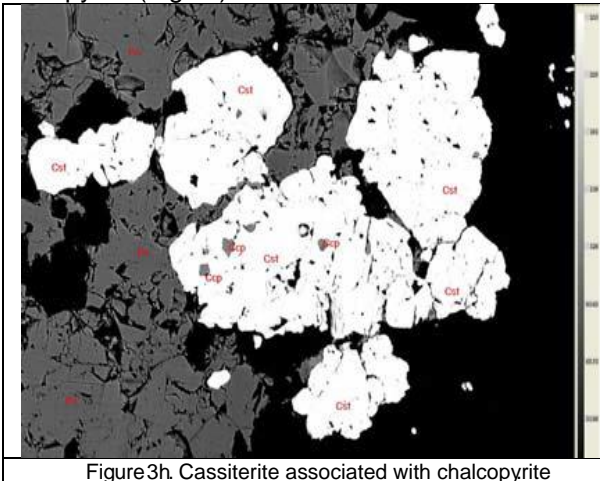


Figure 3h. Cassiterite associated with chalcopyrite

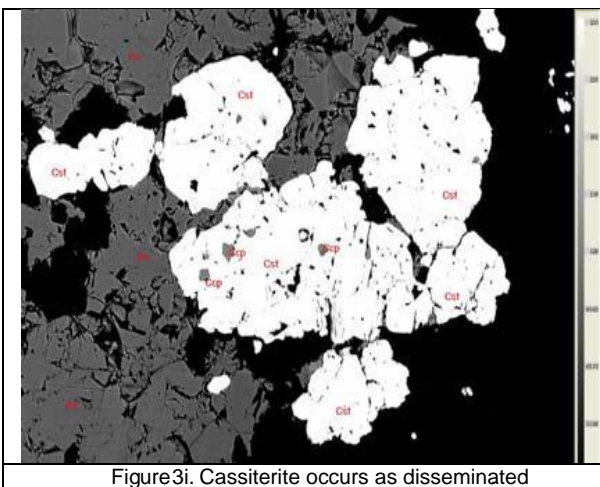


Figure 3i. Cassiterite occurs as disseminated

## VI. FLUID INCLUSION STUDIES

Fluid inclusion parameters in the mineralized quartz veins associated with porphyritic granite and rhyolite

sample were prepared doubly polished thin wafers (thickness  $\sim 0.3 \text{ mm}$ ). Fluid inclusion microthermometry was conducted with the help of a Linkam MDSG600 Heating and Freezing Stage attached with Olympus BX 50 petrological microscope at National Center of Excellence in Geosciences Research (NCEGR), Geological Survey of India (GSI), Bangalore. The stage can operate in a temperature range of  $-198$  to  $600^\circ\text{C}$ . Proper periodic calibration of the stage was done using the pure  $\text{H}_2\text{O}-\text{CO}_2$  synthetic standard inclusions obtained from Linkam.

Fluid Inclusion petrography studies were carried out for the identification of inclusions on the basis of genetic and phase types. The fluid inclusions were identified and broadly grouped them and classified in accordance with the classification principles and techniques outlined by Roedder (1984) Ref. [15] and Luet al (2004) Ref. [16]. In addition, abundance of fluid inclusions was noted following the methods of Touret (2000) Ref. [17]. An attempt was made in the light of new experimental studies by Bodnar et al. (1989) Ref. [18], on the morphology of fluid inclusions to correlate the different textural features of fluid inclusions with equilibration path. The size of the inclusions varies from 1.90 to 58.00  $\mu\text{m}$ . The size of vapour phase of water vapour/CO<sub>2</sub> bubbles varies from 0.39 to 5.50  $\mu\text{m}$ . Based on the phases present, they are grouped into four types: type I inclusions are monophasic carbonic or methane inclusions (type I primary monophasic carbonic and type I<sub>B</sub> methane inclusions), type II primary aqueous carbonic inclusions and type III primary aqueous phase inclusions. Type IV multiphasic inclusions contain the halite crystal with cubes in nature.

The type I<sub>A</sub> inclusions are monophasic carbonic inclusions occur as clusters/isolated and contain only one phase and some are two phases at room temperature (Fig. 4a). The  $\text{CO}_2$  vapour is perfectly circular, spherical and is homogenized into the liquid phase. The type I<sub>B</sub> inclusions are monophasic methane inclusions and occur as clusters/isolated and contain only one phase at room temperature (Fig. 4b) and these methane inclusions are reported first time in this area.

The type II inclusions are less abundant and not so common, these inclusions occur in isolated pattern and contain  $\text{CO}_2$  (liquid)- $\text{CO}_2$  (gas)- $\text{H}_2\text{O}$  (liquid) (Fig. 4c). Type III inclusions are comparatively more abundant than any other inclusions and these inclusions occur as isolated/clustered. (Fig. 4d & e). They are generally small and rounded as well as irregular and contain biphasic  $\text{H}_2\text{O}$ -NaCl inclusions that is homogenized to liquid upon heating. The proportion of vapour phase is typically about 10% to 15% by volume. The type IV inclusions contain aqueous liquid, and vapour and one more solids. The liquid to vapour ratios are similar to those in type I inclusions. The solids are very small in size and anisotropic and generally have high birefringence, although some solids are weakly birefringent or non birefringent (Fig. 4f).

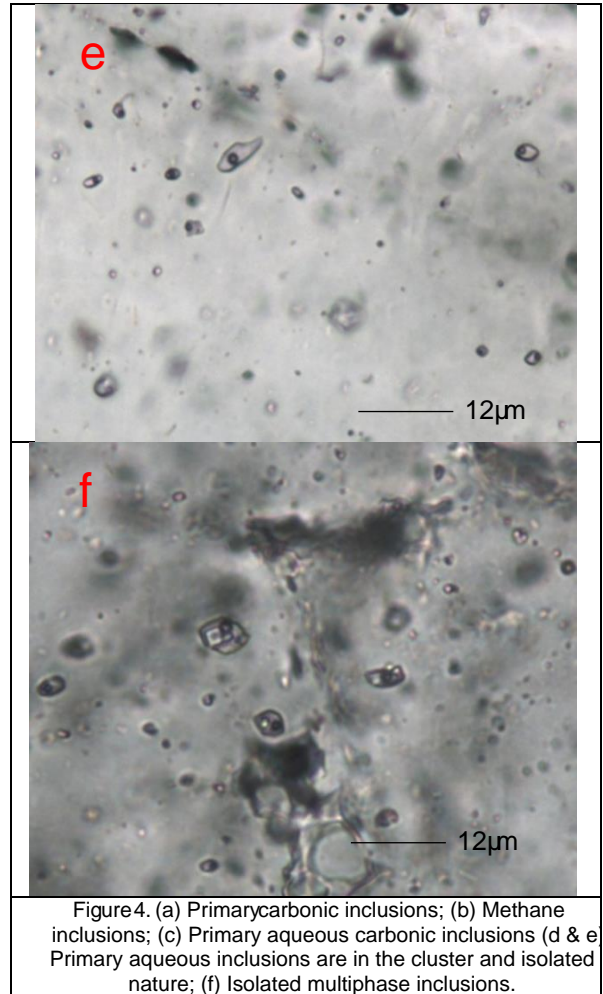
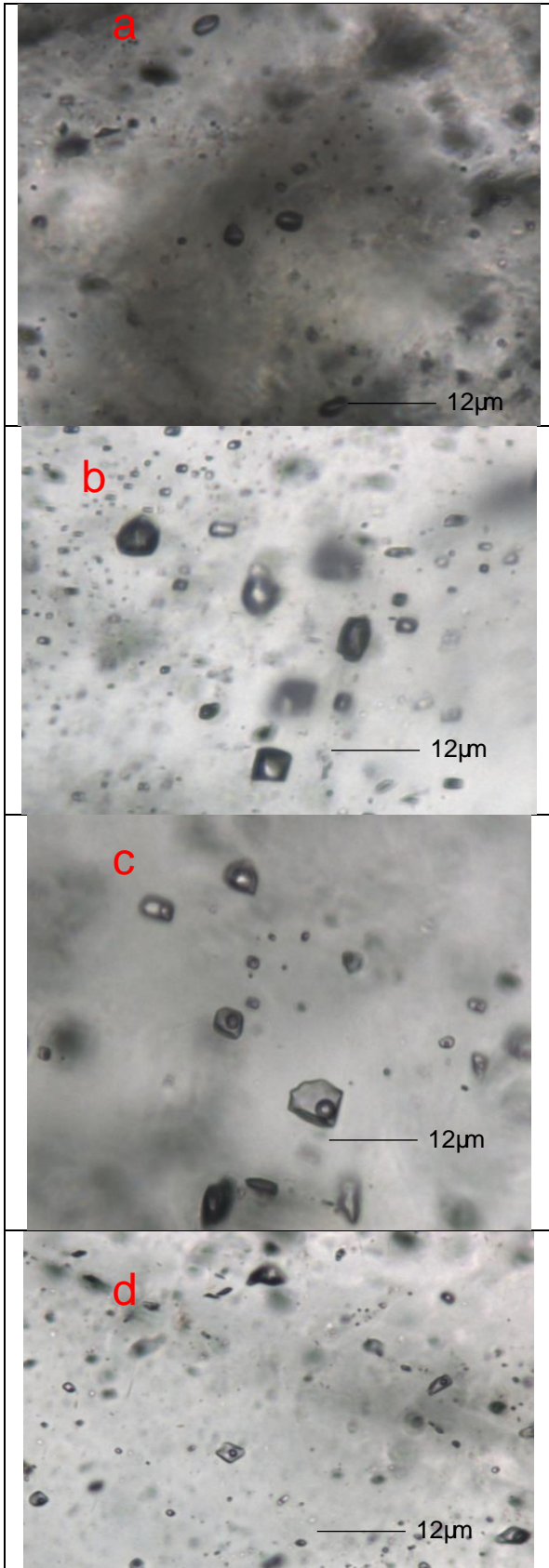


Figure 4. (a) Primary carbonic inclusions; (b) Methane inclusions; (c) Primary aqueous carbonic inclusions (d & e) Primary aqueous inclusions are in the cluster and isolated nature; (f) Isolated multiphase inclusions.

Aqso-le and BULK programs were used to calculate the fluid salinity and density respectively whereas, isochores have been constructed with the help of ISOC program, available with the FLUIDS package (Bakker, 2003). [19]. Above mentioned salinity and density for type III & IV inclusions were calculated using respective equation of state (EOS) of Zhang and Frantz (1987). [20] and Bodnar (1993) Ref. [21] EOS of Duschek et al. (1990) Ref. [22] and Setzmann and Wagner (1998) Ref. [23] were used for type I inclusions to calculate density respectively. However, isochores were constructed using the EOS of Span and Wagner (1996) Ref. [24], Setzmann and Wagner (1998) Ref. [25] and Zhang and Frantz (1987) Ref. [20] for type I, type II and type III inclusions, respectively.

## VII. MICROTHERMOMETRIC MEASUREMENTS

Microthermometric measurements of four types of classified fluid inclusions in mineralized quartz are summarized in Table 1. The type I monophasic inclusions are carbonic and methane, and the melting temperature of methane was at lower temperature and it was confirmed by the Raman spectroscopy (Fig. 5).

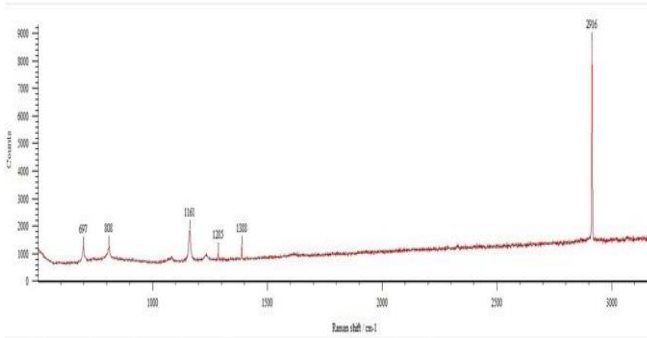


Figure 5. CO<sub>2</sub> and CH<sub>4</sub> peaks detected in the primary monophasic fluid inclusion from Tosham area

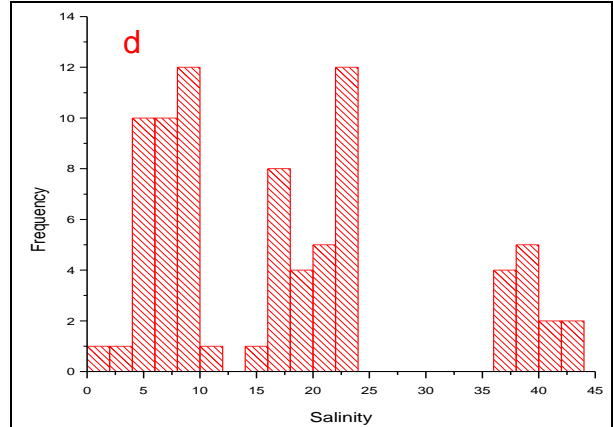
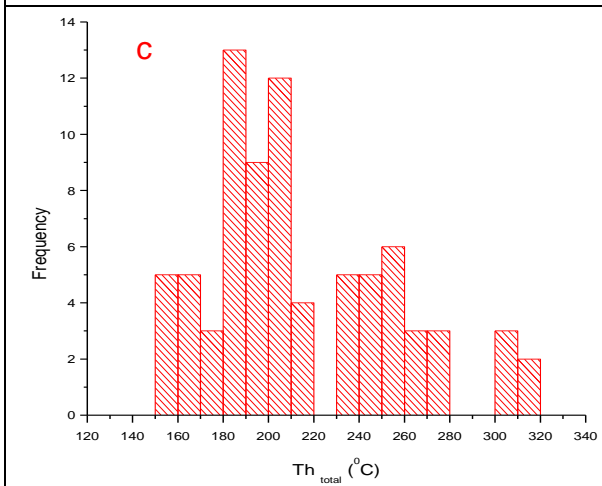
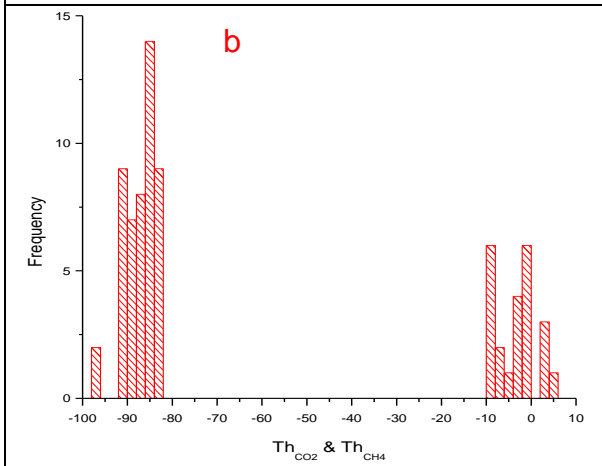
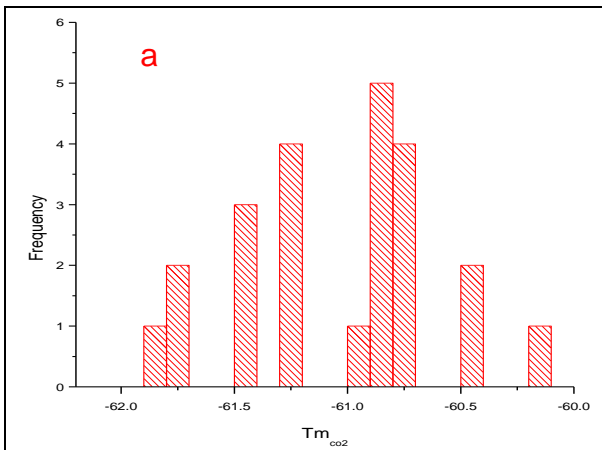


Figure 6 Histograms of the (a)  $T_{mCO_2}$ , (b)  $T_{hCO_2CH_4}$ , (c)  $T_{hTotal}$  and (d) salinity in mineralised quartz veins



The type I inclusions are primary carbonic inclusions formed solid CO<sub>2</sub> upon cooling. The solid CO<sub>2</sub> melt at the temperature between -61.9°C and -60.1°C. In most of the inclusions and in few inclusions the melting temperature observed at lower temperatures -60.5°C, -61.2°C, -61.5°C and -61.9°C. This lowering of melting temperature of CO<sub>2</sub> indicating admixtures of other gases such as CH<sub>4</sub> (van den Kerkhof, 1988; Brown and Lamb, 1989) Ref. [26-27]. The melting temperatures ( $T_{mCO_2}$ ) are graphically illustrated in histogram Fig. 6a. The temperature of homogenized CO<sub>2</sub> into vapour phase at temperature 9.0 to 4.0°C (density varies 0.90 to 0.97 g/cm<sup>3</sup>), which are graphically plotted in histogram Fig. 6b. The primary monophasic methane inclusions melting temperature ( $T_{mCH_4}$ ) was not possible to measure and only CH<sub>4</sub> melting temperature ( $T_{hCH_4}$ ) was measured and varies between -97.0°C to -82.7°C (density varies 0.18 to 0.29 g/cm<sup>3</sup>) which are graphically plotted in histogram (Fig. 6b).

The primary aqueous carbonic inclusions (Type II) inclusions are characterized by the nucleation of a vapour bubble on cooling, consistent with the composition of CO<sub>2</sub>(liquid)+CO<sub>2</sub>(gas)+H<sub>2</sub>O(liquid) +NaCl. These inclusions are coexisting with aqueous rich inclusions, suggesting that the fluid immiscibility might have occurred towards the stage of crystallization (Roedder, 1984) Ref. [15]. The range of homogenization temperature varies from 250 to 310°C. The initial ice melting eutectic temperatures ( $T_e$ ) range from -32 to -50°C with an average of -40.76°C and this suggests that the major component in aqueous phase is NaCl+FeCl<sub>2</sub> in the fluid system (Shepherd et. al., 1988) Ref. [28]. The final melting temperature of ice ranges from -6.9 to -7.2°C (average -5.94°C) corresponding with salinities of 6.22 wt.% to 10.73 wt.% NaCl eq. (average 9.07 wt.% NaCl eq.) following the equations of Bodnar (1993) Ref. [21]. The melting temperature of the CO<sub>2</sub> ( $T_{mCO_2}$ ) ranges from 58.8 to -61.5°C and the homogenization temperature of CO<sub>2</sub> ranges from 16 to 26°C. The CO<sub>2</sub> density of aqueous carbonic inclusion varies from 0.73 to 0.88 g/cm<sup>3</sup>.

The type III inclusions are aqueous inclusions and are frozen at temperatures mainly between -58 to -75°C. The range of homogenization temperature varies from 158 to

245 °C (Fig.6c) and during the heating runs the first melting (eutectic) temperature ( $T_{eu}$ ) has been observed, ranging from -46.8 to -30 °C with an average of -39.61 °C and suggesting that the major component in aqueous phase is  $MgCl_2 \pm FeCl_2$  in the fluid system. The maximum eutectic temperature -46.8 °C may indicate the presence of  $FeCl_2 \pm MgCl_2$  with NaCl and  $H_2O$  (Shepherd et. al., 1985) Ref. [28]. The final melting temperature of ice ( $T_{m(ice)}$ ) ranges from -1.2 to -20.9 °C corresponding salinities of 1.97 to 22.98 wt.% NaCl equivalent. (Fig. 6d). The density of aqueous phase was from 0.86 to 1.05 g/cm<sup>3</sup>. The type IV inclusions are the aqueous multiphase inclusions contain aqueous liquid, a vapour bubble and a halite crystal and these halite crystals show characteristic features of cubic outline. The size of the halite crystals is from 1.5 to 9 μm (in terms of the largest edge) and 2.3 to 6 (diameter), respectively. The homogenization temperature of phase varies from 158 to 271 °C and total granitic melt and early high temperature orthomagmatic homogenisation temperature ranges from 289 to 353 °C. The solid halite crystals melt at very high temperature at 353 °C, this may due to they are accidental trapping and are insignificant in numbers. The salinity ranges from 37.0 to 42.68 wt.% NaCl eq.

The possible presence of NaCl+ $MgCl_2 \pm FeCl_2$  in the brines or complicated mixtures of fluid salt is estimated. The salinity measured in the study area shows high to low salinity ranging from 1.9 wt.% to 42.68 wt.% NaCl eq. and form three clusters (high 37 to 42.68 wt.% NaCl eq. medium 15 to 22.98 wt.% NaCl eq. and low 1.2 wt.% to 10.46 wt.% NaCl eq.). This can also be seen in the plot of salinity vs. homogenisation temperature for the fluid inclusions (Fig. 8).

The fluids of type IV were characterized by have very high salinity inclusions contain halite which is ranging from 37.5 to 39.45 wt.% NaCl equivalent are commonly found in the magmatic hydrothermal fluids (Bodner, 1995; Soman and Srivastava, 2000) Ref. [30&31]. Keppler and Wyllie (1991) Ref. [32] states that if the orthomagmatic fluid was hypersaline, tin would have been strongly partitioning into the aqueous phase upon saturation of the orthomagmatic tin mineralisation would have resulted. The high salinity magmatic fluid suggests orthomagmatic origin for tin is possible at Tosham.

VIII. DISCUSSIONS AND CONCLUSION

Tosham igneous complex are related to the Neoproterozoic acid magmatic event. The anorogenic magmatism of Tosham is attributed to hot spot activity and is due to thermal processes in the asthenosphere (Kochha 1992) Ref. [2]. The Tosham igneous magmatism was triggered by mantle plumes and the release of volatiles from the magma, the melt becomes viscous and during continued advance to higher level it crystallizes as rhyolite. The mineralisation of Sn, W and Cu in the western side of the contact between rhyolite and porphyritic granite. The main ore of tin (cassiterite) occurs as minute grains, specks blades and disseminations in contact between metasedimentary rock with porphyritic granite and in the northern part contact between rhyolite and granite. Other associated ore minerals include wolframite, chalcopryrite, pyrite, stannite, pyrrhotite, cubanite, covellite etc. and EPMA studies confirm the presence of cassiterite, pyrite, chalcopryrite, pyrrhotite and sphalerite. The average concentration of ore reserves of Sn, W and Cu have been estimated at 2.23 million tonnes up to a depth of 237 m below MSL with average grade of 0.28% Sn, 0.18% W and 0.24% Cu (Wokhoo and Prasad, 1989) Ref. [29].

Fluid inclusion studies were carried out on the mineralized quartz veins associated with granite and rhyolite of Tosham igneous complex. The homogenization temperature ( $T_{h(total)}$ ) of type II (250 to 310 °C) and type III (158 to 245 °C) and the estimated P-T condition of temperature was from type III aqueous inclusions range from 310 to 460 °C and pressure was from type I carbonic inclusions ranges from 2100 to 3500 bar (Fig. 7). The first ice melting temperature ranging from 50.0 °C to -30.0 °C suggest the presence of  $FeCl_2 \pm MgCl_2$  and more likely  $CaCl_2$  in the fluid system. The lower the first

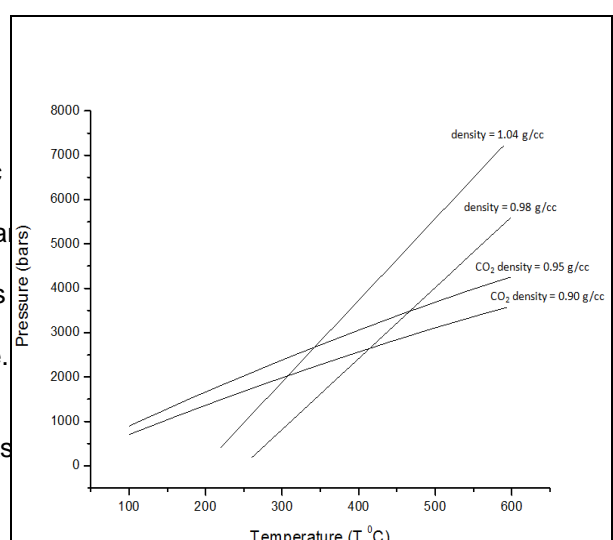


Figure 7. P-T estimation by the intersecting isochores of type I (CO<sub>2</sub> inclusions density) and type II (aqueous inclusions density) inclusions of mineralised quartz veins in Tosham area

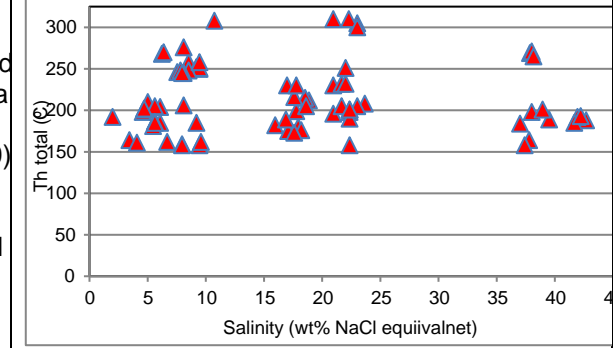


Figure 8. Salinity vs. Temperature of homogenisation ( $T_{h total}$ ) for the inclusions of mineralised quartz veins in Tosham area

The second cluster having medium salinity ranging from 15 to 22.98 wt.% NaCl eq. are characterized by the aqueous carbonic phase (type II) and aqueous phase (type III) inclusions. These fluids characterized by the boiling



fluids after the formation of rhyolite explosion. This continuous guidance and support, motivation and encouragement to carry out this work.

contain fragments of granite/quartzite and these fragments of granite porphyry are attributed to process of fluidisation.

Higgins (1980) Ref. [33] suggested that the dissolved gas content of fluid plays an important role in promoting boiling and coupled to fluid rock reaction appears to have been the major cause of cassiterite precipitation at Tosham.

The type II and type III are homogenized in different ways, the inclusions show higher homogenisation temperatures and lesser salinities in type II compare to type III and numerous studies show that fluid mixing or fluid immiscibility are the dominant mechanisms for the precipitations of tin-tungsten complexes (Wang et al., 2012) Ref. [34]. Bowers and Helgeson show that a homogenous  $\text{CO}_2\text{-H}_2\text{O-NaCl}$  fluid can separate into immiscible  $\text{CO}_2$  rich and  $\text{H}_2\text{O}$  rich fluids due to changes in either temperature or pressure. It is likely that immiscibility was caused initially by gradual cooling [1] followed by a decrease in pressure. The phase separation of the fluids may have been induced by pressure fluctuation and it is evident that vapour rich and liquid rich [2] inclusions are homogenised in the temperature ranges from 250 to 310°C and these temperatures represent the tin-tungsten mineralisation at Tosham.

A large no.  $\text{CH}_4$  inclusions are dominated over the  $\text{CO}_2$  inclusions and are reporting for the first time in this area and confirmed by Raman spectroscopy. The abundant  $\text{CH}_4$  fluid was considered to be one of the diagnostic features of reduced porphyry copper deposit environment (Zhang et. al., 2019) Ref. [35]. The last stage of fluid evolution the temperature (150 to 250°C) and low salinity (1.9 to 9.0 wt.% NaCl equivalent) indicating the mixing of the cooler meteoric waters with the hydrothermal solutions. The decline in salinity and temperature are also due to the loss of  $\text{CO}_2$  and this results deposition of sulphides.

Fluid inclusion studies reveal that ore fluids with high and low salinities in aqueous media with  $\text{CO}_2$  component and the presence of chlorides such as  $\text{FeCl}_2/\text{MgCl}_2$  and  $\text{CaCl}_2$  indicate the involvement of chlorine in transportation of  $\text{Sn}$  to the fluid system. The evaluation of ore forming fluids by high salinity and high temperature with the magmatic hydrothermal activity either by immiscibility or mixing of fluids and evolution of granite/rhyolite induced the fluidisation and the presence of  $\text{CH}_4/\text{CO}_2$  influx might have triggered precipitation  $\text{Sn}$  and copper mineralisation in the area.

#### CONFLICT OF INTEREST

The authors declare no conflict of interest

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#### AUTHOR CONTRIBUTIONS

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