Characteristics of Pegmatite-Related Fluids and Significance to Ore-Forming Processes in the Zhaxikang Pb-Zn-Sb Polymetallic Deposit, Tibet, China

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Abstract: The Zhaxikang Pb-Zn-Sb polymetallic deposit is one of the most important deposits in the newly recognized southern Tibet antimony-gold metallogenic belt. Compared to the porphyry deposits in the Gangdese belt, much less researches have addressed these deposits, and the genesis of the Zhaxikang deposit is still controversial. Based on field investigation, petrographic, microthermometric, Laser Raman Microprobe (LRM) and SEM/EDS analyses of fluid, melt-fluid, melt and solid inclusions in quartz and beryl from pegmatite, this paper documents the characteristics and the evolution of primary magmatic fluid which was genetically related to greisenization, pegmatitization, and silification in the area. The results show that the primary magmatic fluids were derived from unmixing between melt and fluid and underwent a phase separation process soon after the exsolution. The primary magmatic fluids are of low salinity, high temperature, and can be approximated by the H\textsubscript{2}O-\textsubscript{NaCl}-CO\textsubscript{2} system. The presence of Mn-Fe carbonate in melt-fluid inclusions and a Zn-bearing mineral (gahnite) trapped in beryl and in inclusions from pegmatite indicates high Mn, Fe, and Zn concentrations in the parent magma and magmatic fluids, and implies a genetic link between pegmatite and Pb-Zn-Sb mineralization. High B and F concentrations in the parent magma largely lower the solidus of the magma and lead to late fluid exsolution, thus the primary magmatic fluids related to pegmatite have much lower temperature than those in most porphyry systems. Boiling of the primary magmatic fluids leads to high-salinity and high-temperature fluids which have high capacity to transport Pb, Zn and Sb. The decrease in temperature and mixing with fluids from other sources may have caused the precipitation of Pb-Zn-Sn (Au) minerals in the distal fault systems surrounding the causative intrusion.

Key words: Zhaxikang Pb-Zn-Sb deposit, South Tibte Sb-Au metallogenic belt, fluid inclusion, pegmatite, ore-forming process

1 Introduction

The Himalayan-Tibetan orogenic belt provides a good opportunity for the research of Cenozoic orogeny process and metallogeny, especially for metallogeny during the continent-continent collision process. Convergence between the India and Asia plates involved complex processes including subduction of the Neotethyan ocean (Andean type subduction), the accretion of India continent, and the continent-continent collision which started at about ca. 65 Ma (Mo et al., 2003). In response to the subduction, collision and post-collision convergence are a series of tectono-magmatic events recorded in the Bangonghu-Nuijiang and the Gangdese magmatic belts. Various mineral deposits were formed during these processes, including subduction related porphyry Cu (Au) and epithermal Au (Cu) deposits (e.g., the Duobuzha deposit in the Ali area), collision related porphyry and

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skarn deposits (e.g., Fe-Pb-Zn skarn deposits in the north Gangdese belt, and the Yulong porphyry Cu deposit in eastern Tibet), and post-collision related porphyry Cu-Mo (Au) deposits in the Gangdese belt (e.g., the Chongjiang, Qulong, and Jiama deposits) (Hou and Yang, 2009 and the references there in). A number of papers, both in Chinese and in English, have been published about the geology and geochemistry of the deposits in the Gangdese belt, Yulong belt, and Bangonghu-Nuijiang belt in the last two decades. Compared to these well studied metallogenic belts, the newly recognized southern Tibet antimony – gold metallogenic belt has received much less research.

The Zhaxikang Pb-Zn-Sb polymetallic deposit, which is located in 60 km west of Longzi county, Tibet, is one of the most important deposits in the southern Tibet antimony-gold metallogenic belt (Yang et al., 2006), with a total confirmed metal resource of 636720 t of Zn, 392090 t of Pb, 108346 t of Sb and 1399.17 t of Ag (Chinese land and Resources News, 2013, May, 5). Limited geological and geochemical data have been reported for this deposit in recent years (e.g., Wang et al., 2011; Liang et al., 2013; Lin et al., 2013), but it remains controversial about the ore genesis, the characteristics of the ore-forming fluids, and the link between Pb-Zn-Sb mineralization and pegmatites as well as two mica granites in this area. Zhu et al. (2012) proposed that the deposit is a moderate-low temperature hydrothermal deposit formed from circulation of basinal fluids and controlled by structures, and Wang et al. (2011) emphasized the link with sedimentary rocks and the multi-stage nature of mineralization, as also suggested by Liang et al. (2014). Based on Si and O isotopes of chert and H-O isotopes of fluid inclusions in chert-related quartz in the deposit area, Meng et al. (2008) suggested that the Sb mineralization in Zhaxikang took place in a hot-spring environment. Zheng et al. (2012) and Sun et al. (2014) believe that the Zhaxikang deposit experienced Late Jurassic SEDEX type mineralization in a passive continental margin environment and the Miocene epithermal type mineralization. Li et al. (2014) and Zhang et al. (2014) believe that Sb, As, Ag, and S in the Zhaxikang deposit were derived from the host strata (the Ridang Formation), but Pb and Zn were sourced from the metamorphic rocks (the Luguangangri Group) and related leucogranites in the basement. The enrichment of ore-forming elements in Ridang formation is likely caused by seafloor hydrothermal activity (Cheng et al., 2014). Based on the chemistry of sulfide minerals from the ores, Lin et al. (2013) proposed that the Zhaxikang deposit has a genetic link with magmatic fluids, and Wang et al. (2012) suggested that the Zhaxikang deposit is a mesothermal deposit controlled both by structures and magmatism.

Greisens and pegmatites are well developed in the deposit area, and are spatially associated with two-mica granites. The potential genetic relationship between magmatism and the Pb-Zn-Sb mineralization may be revealed by studying the fluid inclusions in the pegmatites and comparing them to those found in the ore-related minerals, which constitutes the main subject of study of this paper.

2 Regional Geologic Setting and Ore Deposit Geology

The Zhaxikang deposit is located in southern Tibet, about 300 km Southeast of Lhasa (Fig. 1). Tectonically,
the Zhaxikang deposit is located in the South Tibetan Detachment System of the Himalayan-Tibetan orogenic belt, the collisional zone between Asia and India continents. The Himalayan-Tibetan orogenic belt has undergone a complex evolution from the subduction of Indian oceanic crust underneath the Euro-Asia plate starting in late Cretaceous, through the closure of the Neo-Tethys ocean, to the collision between Asia and India continent at about 65 Ma (Mo et al., 2003). The Himalayan-Tibetan orogenic belt includes the Lesser Himalaya (LHS), High Himalaya (HHS) and Tethys Himalaya (THS) units. The South Tibetan Detachment System (STD) refers to the area in the north slope of the Himalaya, south of the Yaluzangbu suture, characterized by strong deformation and separated from the underlying great Himalaya series by normal faults (Chen and Liu, 1996). It is situated between the High Himalaya and Tethys Himalaya (Fig. 1, Yang et al, 2011). A large number of Pb-Zn, Au, Au-Sb and Sb deposits have been reported in this belt including the Zhaxikang Pb-Zn polymetallic deposit, Shalagang Sb deposit, Mayum Au deposit, Mazhala Sb-Au deposit.

Most of the Zhaxikang area is covered by the Lower Jurassic Ridang Formation (J1r) (Fig. 2), which is composed of black shale (locally altered to carbonaceous slate), argillaceous limestone and sandstone with chert and tuff interlayers. The intrusive rocks in the area include rhyolite porphyry, two-mica granite dikes/stocks, granite porphyry and minor diabase dikes (Huayu mining Co. Ltd and Chengdu center of geological survey, 2012; Tang et al., 2014). Two-mica granite occurs as small stocks or dikes outcropping in the north and south of the deposit. Petrographic studies show that the two-mica granite has fine-grained to porphyritic texture, with a mineral

Fig. 2. Geological map of the Zhaxikang Pb-Zn-Sb deposit and surrounding area.
assemblage of K-feldspar, quartz, muscovite, biotite, and minor zircon, apatite, and ilmenite as accessory minerals. The structures in the deposit area are dominated by faults trending NS, NE and NW. The mineralization occurs mainly in the Ridang Formation and is controlled by NS- and NE-trending high-angle normal faults (Huayu mining Co. Ltd and Chengdu center of geological survey, 2012).

Field observations and petrographic studies indicate that the Zhaxikang area is affected by various alterations including Fe-Mn carbonatization, silicification, chloritization, limonitization, pyritization, argillation, sericitization, pegmatation, and greisenization. The Pb-Zn-Sb mineralization is closely related to Fe-Mn carbonatization, silicification and chloritization. The greisenization and pegmatitization occurs in the north and south of the deposit area, in the distal zone away from the orebodies. The pegmatites in the Cuonadong two-mica granite in the south of the Zhaxikang area have been referred to as tourmaline-muscovite granites. The pegmatite occurs as veins (Fig. 3a) and dikes in the two-mica granite, or as irregularly shaped bodies in metamorphic rocks in the basement (Fig. 3b). Quartz-tourmaline vein/dikes were also observed (Fig. 3c). The mineral assemblage of pegmatites includes feldspar, quartz, tourmaline, beryl (Fig. 3d), ilmenite, muscovite, biotite, and garnet. Silicification is well developed in the Zhaxikang area, and is manifested as greisenization, quartz-sericite alteration, to quartz-chlorite alteration from the pegmatites to the deposit.

The dominant mineralization styles are structure-controlled veins and stockworks, with minor breccia-style mineralization. Based on crosscutting relationships of veins and petrographic studies, three ore-forming stages were recognized in the deposit, including 1) the quartz-chlorite stage characterized by a mineral assemblage of quartz, chlorite, with minor sericite and pyrite, 2) the carbonate-sulfide stage with a mineral assemblage of galena, sphalerite, Mn-Fe carbonate (Mn-siderite, Fe-rhodochrosite, and rhodochrosite), stibnite, boulangerite, chalcopyrite, pyhrotite, and arsenopyrite, and 3) the quartz-stibnite stage with a mineral assemblage of quartz, boulangerite, stibnite, calcite, and Mn-calcite. Based on

![Fig. 3. Photographs of pegmatite outcrops in the Zhaxikang area.](image)

(a), pegmatite vein in two-mica granite; (b), pegmatite; (c), quartz-tourmaline veins; (d), beryl in pegmatite; Q-quartz; Be-beryl; Fsp-feldspar; Tur-tourmaline; Mus-muscovite.
petrographic, ore microscopic and scanning electron microscope/ Energy-dispersive spectroscopy (SEM/EDS) analyses, the metallic minerals are mainly pyrite (Figs. 4a and 4b), sphalerite (Figs. 4a and 4b), galena (Fig. 4a), stibnite (Fig. 4d), tetrahedrite (Fig. 4b), chalcopyrite (Figs. 4b and 4c), boulangerite, zincenite, bouronite and freibergite, and the main gangue minerals are Fe-Mn carbonate, quartz, calcite, sericite, and chlorite.

3 Fluid Inclusion Studies

3.1 Samples and analytical methods

The minerals investigated for this study include quartz and beryl from pegmatite. Microthermometry was undertaken using a Linkam TH5600 heating-freezing stage, with a measurable temperature range between \(-196^\circ\) and \(+600^\circ\)C in the Department of Resources Engineering of USTB, University of Science and Technology Beijing. The stage was calibrated with synthetic fluid inclusions with known phase change temperatures, and the precision was better than \(\pm 0.2^\circ\)C for measurements of homogenization temperatures of CO\(_2\) and other phase changes at lower temperatures, and better than 2\(^\circ\)C for other measurements at higher temperatures. Laser Ramam Microprobe analysis (LRM) was carried out at the Analytical Laboratory of the Beijing Research Institute of Uranium Geology, using a LABHR-VIS LabRAM HR800 Laser Raman Spectroscope with a laser wave-length of 532 nm. SEM/EDS analyses were performed at the State Key Laboratory of Advanced Metals and Materials of the University of Science and Technology Beijing, using a FEI Quanta 600 MLA ESEM equipped with an EDAX Genesis 7000 EDS system, and a ZEISS SUPRA55 SEM equipped with Thermo Noran System 6 EDS system.

3.2 Petrography of fluid inclusions

The inclusions in beryl and quartz from pegmatite occur as isolated individuals, clusters, and trails. Most of them occur as clusters. Those that may be primary or
Four types of inclusions were distinguished based on phase assemblages at room temperature, i.e., solid inclusions (type S), melt inclusions (type M), melt-fluid inclusions (type ML), and fluid inclusions. The fluid inclusions were subdivided into four sub-types, i.e., aqueous-CO₂ (type AC), CO₂ (type C), aqueous-CO₂ inclusions containing solids (type ACS), and aqueous inclusions with halite daughter mineral (type ADV). The characteristics of each type and sub-type are described below.

Solid inclusions occur as octahedral shaped crystals (Fig. 5a) and irregularly shaped solid phases (not glass) in beryl. The solid inclusions include cristobalite, quartz, muscovite and garnhite (ZnAl₂O₄), as revealed by LRM and SEM-EDS, and other unidentified minerals.

Melt inclusions are found in beryl and comprise one or more daughter minerals and glass, with or without a bubble at room temperature (Fig. 5b). Melt-fluid inclusions also occur in beryl, and contain a CO₂ vapor, an aqueous liquid, and a glass phase (Fig. 5b), with or without solid minerals at room temperature.

CO₂-rich fluid inclusion (types AC, A and ACS) occur both in quartz and beryl. Type AC inclusions consist of an aqueous liquid and a CO₂ vapor (Fig. 5d), and type C inclusions comprise of just a CO₂ vapor (Fig. 5c), whereas type ACS inclusions contain one or more solid phases in addition to an aqueous liquid and a CO₂ vapor (Figs. 5b and 5c). Type AC, A, ACS, ML and M inclusions coexist in beryl.

Halite-bearing fluid inclusions (type ADV) are similar to the type ACS inclusions in that they all contain an aqueous liquid, a CO₂ vapor, and one or more solid phases, but type ADV inclusions contain a halite daughter mineral (Fig. 5f), and type ACS inclusions do not. Type ADV inclusions occur in quartz and coexist with type AC and type C inclusions.

3.3 Microthermometric results

Microthermometric measurements have been carried out for type AC, ACS, C and ADV inclusions (Table 1). The microthermometry for melt and melt-fluid inclusions is currently in progress, and no results have been obtained so far.

The melting temperatures of solid CO₂ (Tₘ,CO₂) for type AC, ACS and C inclusions range from −58.1 to −59.6°C, suggesting that the vapor is dominated by CO₂, but other volatiles are also present. The clathrate melting temperatures (Tₘ,clath) are in the range of 4.1 – 9.9°C, and the estimated salinities are 0.2wt% NaCl<sub>eq</sub> – 7.9wt% NaCl<sub>eq</sub>. The partial homogenization temperatures of CO₂ phase (T<sub>h,CO₂</sub>) vary from 22 to 29.9°C (homogenized to vapor phase). The total homogenization temperatures of AC-type inclusions (T<sub>h,total</sub>) are from 298 to 457°C. Halite melting temperatures of ADV-type fluid inclusions in quartz are in the range of 128–214°C, with the salinities being 29.0wt% NaCl<sub>eq</sub> – 32.5wt% NaCl<sub>eq</sub> and the total homogenization temperatures varying from 205 to 351°C.

3.4 LRM and SEM results

The LRM spectra indicate that some solid inclusions in beryl are cristobalite (417 nm) (Fig. 6a) together with quartz (465 nm) (Fig. 6b), and some solid inclusions cannot be identified with LRM.

The LRM results for the vapor phase in melt-fluid and fluid inclusions (types ML, AC, C and ADV) show that the vapor phase in both ML and fluid inclusions is dominated by CO₂, with minor H₂O, CH₄ and N₂ (Figs. 6c and 6d). The aqueous phase is dominated by water (Fig. 6e). LRM results for the daughter phases in ML and ACS inclusions include cristobalite, rhodochrosite (Fig. 6f), quartz and garnhite. Microthermometric and LRM results indicate that the daughter phases in ADV inclusions are dominated by halite.

The SEM/EDS results for the solid inclusions in beryl also confirmed that the trapped mineral in beryl include cristobalite or quartz, muscovite and garnhite (ZnAl₂O₄) (Fig. 7a and 7b). Garnhite is also commonly found as a solid phase within fluid inclusions in beryl.

4 Discussions

Most pegmatite formed in volatile-rich melt, and

| Table 1 Microthermometric results of fluid inclusions in quartz and beryl |
|-----------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Host mineral  | Sample number | Type | Tₘ,CO₂ (°C) | Tₘ,clath (°C) | Tₘ,CO₂ (°C) | Tₘ,clath (°C) | Tₘ,CO₂ (°C) | Salinites (wt% NaCl<sub>eq</sub>) |
| quartz | ZK11097 | AC | −58.1 – −59.6 (18) | 5.7 – 9.2 (8) | 26.5 – 29.8 (19) | 352 – 425 (18) | 16.6 – 7.9 |
| quartz | ZK1107 | AC | −58.3 – −59.0 (16) | 4.1 – 9.6 (8) | 27.3 – 29.9 (16) | 308 – 457 (15) | 30.4 – 32.5 |
| beryl | ZK1106-2 | AC | −58.0 – −59.4 (14) | 7.1 – 9.9 (11) | 22.0 – 27.5 (2) | 310 – 378 (9) | 0.2 – 5.5 |
| beryl | ZK1106-4 | ACS | −58.4 – −58.9 (8) | 7.0 – 9.9 (12) | 26.5 – 27.8 (3) | 310 – 360 (12) | 0.2 – 5.7 |
| *No data available or the data can’t be acquired.*
Fig. 5. Photomicrographs of fluid inclusions in beryl and quartz in pegmatite.

(a), A solid inclusion in beryl; (b), Melt-fluid inclusions in beryl; (c), Aqueous-CO$_2$ inclusions containing solid phases in beryl; (d), An aqueous-CO$_2$ inclusion in beryl; (e), A CO$_2$ inclusion in beryl; f, A halite-bearing aqueous-CO$_2$ inclusions in quartz. S$_1$-cristobalite; S$_2$-quartz; S$_3$-rhodochrosite; S$_4$-halite; V-vapor phase; L$_{H2O}$-aqueous phase; G-glass phase; Be-beryl; Q-quartz.

recorded the transition from melt to fluid (Roedder, 1992). The existence of early crystalized cristobalite and gahnite in beryl indicate that the parent magma of the pegmatite was of very high temperature. Cristobalite occurs as β-cristobalite at high temperature which is stable at temperatures from 1470°C to the melting point (1728°C) (Gaines et al., 1997). Cristobalite can maintain metastable state at much lower temperatures, and experience a displacive phase transformation to α-cristobalite at 268°C for highly ordered, pure cristobalite or as lower as 175°C where a high level impurities exist (Gaines et al., 1997). However, under most natural conditions, cristobalite forms in metastable state from amorphous silica at temperatures from 800 to 1300°C, below its stability field.
Fig. 6. Raman spectra of solid, melt-fluid and fluid inclusions in beryl and quartz.
(a), Cristobalite in beryl; (b), Quartz in beryl; (c), Vapor phase of an ML inclusion in beryl; (d), Aqueous phase of a ML inclusion in beryl; (e), Rhodonite in ACS inclusion in beryl; (f), Vapor phase of an AC inclusion in quartz.

(Jones, et al., 1972; Darling, et al., 1997; Xiao et al., 2003).

Field observation and petrographic results indicate that tourmaline is abundant in pegmatite and pegmatitized two-mica granite in the study area, suggesting high B and F contents in the parent magma. High B and F concentrations can lower the solidus of the magma, and lead to long-lived magmatism, which allows evolution of magmatic fluid to occur at temperatures lower than most magmatic systems.

Petrographic studies suggest that beryl crystallized earlier than quartz in pegmatite. The coexistence of type M, ML, AC, ACS and C inclusions in beryl implies that beryl crystallized in the transition from melt to fluid, and the primary magmatic fluid in this stage was enriched in CO$_2$. This is best manifested by the CO$_2$-rich fluid phase in the ML inclusions. The LRM and microthermometric results show that the primary magmatic fluid is a high-temperature, low-salinity, CO$_2$-rich fluid, with minor CH$_4$ and N$_2$.

The absence of type M and ML inclusions in the paragenetically late quartz in pegmatite suggests that quartz was precipitated below the solidus of the magma, and the occurrence of type ADV inclusions implies that
some high-salinity fluids were developed in this stage of magmatic-hydrothermal evolution. The coexistence of type AC, C and ADV fluid inclusions in quartz may reflect phase separation from an original aqueous-carbonic fluid into two immiscible phases, i.e., a CO$_2$-rich vapor phase (represented by type C inclusions) and a high-salinity liquid phase (represented by type ADV inclusions). During the phase separation or unmixing process, base metals are preferentially partitioned into the aqueous phase, because Pb and Zn are favorably transported as Cl-complexes in brine (Heinrich et al., 1999). The metal-bearing high salinity fluids may have migrated outward along fault systems, and metal sulfides may be precipitated due to temperature drop or mixing with fluids from other sources, such as underground water and hot-spring water which may have lowered the salinity or changed the pH of the fluids (e.g. Wilkinson, 2001, Boroejić Šoštarić et al., 2013).

The Fe-Mn carbonate (e.g., rhodochrosite) and cristobalite daughter phases in type ML and ACS inclusions imply high solubilities of silica, manganese and iron in the primary magmatic fluid. The existence of gahnite (ZnAl$_2$O$_4$) in fluid inclusions in beryl indicates that the parent melt and primary magmatic fluid contained high concentrations of Zn. Therefore, the magmatic fluids related to the pegmatite in the study area have the potential to provide large amounts of base metals for the formation of the Zhaxikang Pb-Zn-Sb polymetallic deposit. Interestingly, rhodochrosite, which occurs as a daughter phase in the type ML and ACS inclusions, is also well developed in the main ore-forming stage in the Zhaxikang deposit. Furthermore, previous studies of fluid inclusions from the main ore-forming stage minerals of the Zhaxikang deposit (Zhu et al., 2012) also indicate the presence of CO$_2$ and CH$_4$ in the ore-forming fluids. Putting these together, it is believed that magmatic fluids, as recorded by fluid inclusions in the pegmatite, played an important role in the formation of the Zhaxikang Pb-Zn-Sb polymetallic deposit.

5 Conclusions

(1) The primary magmatic fluids which were genetically related to greisenization and pegmatitization in the Zhaxikang area, derived from unmixing between melt and fluid in the late magmatic stage, are characterized by the H$_2$O-NaCl-CO$_2$ system with high temperatures and low salinities.

(2) The primary magmatic fluids underwent a phase separation process soon after the exsolution, which
resulted in a low-salinity CO₂-rich fluid and high-salinity fluid. Base metals were preferentially partitioned in the high-salinity fluids, which may have migrated away from the magmatic systems and precipitated ores due to temperature drop or mixing with fluids from other sources.

(3) The potentially high concentrations of base metals in the magmatic fluids, as reflected by gahnite (ZnAl₂O₄) in fluid inclusions in beryl, the development of rhodochrosite both as a daughter mineral in inclusions in beryl and as an important mineral in the main ore stage of the Zhaxikang Pb-Zn-Sb deposit, and the presence of CO₂ in both the fluid inclusions in the pegmatite and in the Zhaxikang deposit, suggest that the Pb-Zn-Sb mineralization may be genetically related to magmatic fluids.

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