Fluid Characteristics and Evolutionary History of the Zhawulong Granitic Pegmatite Lithium Deposit, Ganzi-Songpan Region, Southwestern China

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Abstract: The Zhawulong granitic pegmatite lithium deposit is located in the Ganzi-Songpan orogenic belt. Fluid inclusions in the spodumene, and coexisting quartz from this deposit, have been evaluated with respect to the cooling path and fluid evolution within albite–spodumene pegmatite. There are three distinguishable types of fluid inclusions: crystal-rich, CO₂–NaCl–H₂O, and NaCl–H₂O. At more than 500 °C and 350 MPa, crystal-rich fluid inclusions were captured during the pegmatitic magma-hydrothermal transition stage, characterized by a dense hydrous alkali borosilicate fluid with a carbonate component. Between 412 °C and 278 °C, CO₂–NaCl–H₂O fluid inclusions developed in spodumene (I) and quartz (II) with low salinity (3.3–11.9 wt.% NaCl equivalent) and high volatile content, conditions representing the boundary between the transition stage and the hydrothermal stage. The subsequent NaCl–H₂O fluid inclusions from the hydrothermal stage, between 189 °C and 302 °C, have low salinity (1.1–13.9 wt.% NaCl equivalent). The various types of fluid inclusions reveal the P–T conditions of pegmatite formation, which marks the transition process from magmatic to hydrothermal. The ore-forming fluids from the Zhawulong deposit have many of the same characteristics as those from the Jiajika lithium deposit. The ore-forming fluid not only provided materials to crystallize rare metal minerals, such as spodumene and beryl, but also had the ideal conditions for the growth of ore minerals. Therefore, this area has favorable conditions for lithium enrichment and excellent prospection potential.

Keywords: granitic pegmatite; Zhawulong; lithium deposit; fluid inclusions; rare metal.

1 Introduction

Granitic pegmatites are known for reserving rare minerals and are easy to exploit for economic interests (Yuan et al., 1987; Chen et al., 1990; Fu et al., 2015; Wang et al., 2016). Many studies indicate that pegmatite rare metal deposits tend to undergo complex ore-forming processes (e.g., Jahns and Burnham, 1969; Černý et al., 1991; Sirbescu and Nabelek, 2003; Rickers et al., 2006; Simons and Webber, 2008; Thomas and Davidson, 2016; London, 2018). One potentially valuable means of understanding the ore-forming process is through examining the abundant fluid inclusions within pegmatite minerals (e.g., London, 1986; Webster et al., 1997; Thomas et al., 2000, 2003, 2005; Thomas and Webster, 2000; Audéat and Pettke, 2003). Fluid inclusions often provide direct temperature and pressure information during mineral crystallization (Roedder, 1984, 2003). Therefore, fluid inclusions can give information about the migration, enrichment, and ore-forming potential of granitic pegmatite lithium deposits (London, 2008; Stefanova et al., 2014). Previous fluid inclusion studies in pegmatites were conducted in pegmatite rare metal deposits to reveal the transition process from magma to

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hydrothermal (e.g., London, 1984, 1986, 2018; Lu et al., 1996; Fuertes-Fuente and Martin-Izard, 1998; Fuertes-Fuente et al., 2000; Sirbescu and Nabelek, 2003; Rickers et al., 2006; Li et al., 2007; Simmons and Webber, 2008; Thomas et al., 2005, 2016; Li and Chou, 2016, 2017). However, there are few studies on the ore-forming fluid properties and P–T path of the transition process. This may be since fluid inclusions are rarely represented as a magma-hydrothermal transition of pegmatite because of hydrothermal and/or metamorphism processes that overprint the fluid transition history. Spodumene, the host for ore-forming fluid inclusions, is susceptible to destruction by late hydrothermal alteration. A well-preserved spodumene specimen, with relatively complete differentiation, can solve this problem. Two types of fluid inclusions hosted in spodumene can be distinguished from the zoned pegmatite (e.g., London, 1984, 1986, 1995, 1996, 2018; Černý et al., 1991; Lu et al., 1996; Sirbescu and Nabelek, 2003; Rickers et al., 2006; Thomas et al., 2005, 2016; Li and Chou, 2016, 2017): (1) crystal-rich fluid inclusions; and (2) CO$_2$-NaCl–H$_2$O fluid inclusions. With the experimental calibration of the lithium aluminosilicate phase diagram (London, 1984), detailed studies combined the diagram with fluid inclusion data to investigate the P–T conditions and fluid evolution in some pegmatite deposits (London, 1984, 1996; Lu et al., 1996; Sirbescu and Nabelek, 2003; Li and Chou, 2016, 2017). However, these studies concentrated on the systematics of fluid inclusion populations and the ore-forming process rather than on a comprehensive interpretation of fluid evolution.

The granitic pegmatite rare metal deposits in China are mainly distributed in the Altai metallogenic belt in Xinjiang, the Songpan-Ganzi metallogenic belt in Western Sichuan, and the Nanling metallogenic belt in southern China (Li et al., 2007, 2014). The Songpan-Ganzi metallogenic belt has attracted attention because of its large lithium reserves (more than 2.5 million tons of Li2O) and great prospecting potential (Wang and Fu, 2013; Hao et al., 2015; Ju et al., 2016; Wang et al., 2016). The Zhawulong deposit is a large, granitic, pegmatite lithium deposit in the Songpan-Ganzi metallogenic belt. There are different generations of spodumene and coexisting quartz in the Zhawulong deposit. Various types of fluid inclusions occur within these minerals, representing a series of fluid inclusion events that have probably undergone a comparatively complete differentiation process. Therefore, this deposit is an ideal place to constrain the P–T conditions transition from magma to hydrothermal of granitic pegmatite rare metal deposits. In this paper, a systematic fluid inclusion study of the Zhawulong lithium deposit is carried out to define the emplacement conditions, cooling histories, and fluid evolution in this pegmatite. A detailed comparison of P–T conditions between this deposit and typical granite pegmatite lithium deposits (Jiajika in Sichuan, Koktokay in Xinjiang, etc.) is presented to describe the genesis of pegmatite and its associated rare metal deposits.

2. Regional geological background

The Songpan-Ganzi orogenic belt is one of the most important rare metal metallogenic belts in China. It lies in southwestern China and spans Sichuan and Qinghai provinces, adjacent to the Tarim Block to the north, the Qiangtang-Changdu Block on the outer margin of what was formerly the Gondwana continent to the east, and the Yangtze Block to the southeast (Li et al., 2007; Liu et al., 2016). Substantial lithium, beryllium, niobium, tantalum, and other rare element resources are found in the granite pegmatite in this area. The newly discovered deposits (spots) are mainly distributed in the eastern margin of this orogenic belt, such as the Pingwu, Malkang, Danba, Yajiang, and Jiulong deposits (Zhao et al., 2015; Wu et al., 2016), mainly including the Jiajika large lithium ore field, the Keeryin large lithium ore field, and the Zhawulong large lithium deposit. The strata are early Triassic mudstones and sandstones in the pegmatite ore field of the Songpan-Ganzi rare metal metallogenic belt. They developed into various slates, phyllites, and schists by regional metamorphism and thermocontact. The two-mica granites of the early Triassic age are especially developed, having a close relation with mineralization, such as in Jiajika, Zhawulong, and Keeryin. The two-mica granite is mostly irregular with an exposed area ranging from several square kilometers to more than 100 square kilometers. During magmatism, the wall rocks underwent multistage metamorphism, which formed five distinct metamorphic zones surrounding the two-mica granite (from inner to outer): the diopside, staurolite, andalusite-staurolite, andalusite, and biotite zones. Later, pegmatite dikes developed surrounding the granite (Li et al., 2013; Wang et al., 2015; Hao et al.,
2015).

3. Deposit geology

The Zhawulong lithium deposit is located in Kayaji, 42 km away from Xiayi in Ganzi Autonomous Prefecture, Sichuan Province. The western part of this deposit is in Chenduo County in Yushu Autonomous Prefecture, Qinghai Province (Fig. 1). The outcropped strata are early Triassic sandstone interbedded with slates, which are moderately and shallowly metamorphic rocks such as biotite quartz schist, dimica quartz schist, andalusite, and cruciferous quartz schist formed by regional and thermocontact metamorphism. The orebody was predominantly controlled by the Kayaji anticline. The small folds on the anticline’s two wings are well developed. The fold axis is NW–SW–SEE (for east-southeast). The dip of the two flanks is gentle (approximately 15°–25°), while the dip of the northern flank is steep (approximately 36°–57°). The Yanshanian Kayaji two-mica granites intrude along the Kayaji anticline core. Well-developed pegmatites surround the granite body.

A total of 111 pegmatite dikes of various sizes were identified in the Zhawulong deposit, with lengths of 2–10 km and widths of 0.5–80 m. Pegmatite veins were irregularly shaped, formed mostly in veins and a few in lenticular shapes, with obvious horizontal zoning. Based on the characteristics of different typical minerals, pegmatite dikes can be divided into five types: the microcline, microcline–albite, albite, albite–spodumene, and lepidolite (muscovite) types. These pegmatites have different degrees of differentiation. The microcline pegmatites were generally poorly differentiated with mostly reticulated, lenticular, or massive shape. In some cases, microclin pegmatites occurred in a transitional relationship with two-mica granite as pegmatite-like rocks. The microcline–albite pegmatites were mainly composed of microcline and coarse, white quartz without mineralization. Moreover, a large number of tourmaline can be seen in the microcline–albite pegmatites without obvious differentiation characteristics. The albite–spodumene pegmatites generally had good differentiation characteristics, and some of the large ones had full differentiation characteristics. The lepidolite (muscovite) pegmatite veins are distributed on the margin or outside of the albite–spodumene along with fine feldspar, quartz, and muscovite.

The No. 97, 100, and 108 veins are albite–spodumene pegmatite veins with a length of approximate 50 m and widths of 3–5 m. The veins are zoned to some extent. They can be divided, roughly, into an inner albite–spodumene belt and an outer microcline–albite belt. The main body is the albite–spodumene belt (approximately 90% of the whole pegmatite vein). The albite–spodumene belt is mainly composed of spodumene, quartz, albite, and muscovite (Fig. 2A). Spodumene is mainly divided into two generations in the albite–spodumene belt. The early stage I spodumene is light green or gray-white, 1–10 cm long and 0.5–1 cm wide, coexisting with quartz and albite with sharply contacting boundaries (Fig. 2B). The late stage II spodumene is coarse-grained as anhedral or subhedral crystals, approximately 0.5–1 cm long and 0.5–2 mm wide and mostly filled in with albite and other minerals (Fig. 2C). The quartz in the albite–spodumene belt can be divided into two stages. In stage I, the quartz grows irregularly in the interstitial space of spodumene (Fig. 2A, B, C), which suggests the quartz at stage I is obviously younger than the spodumene at stage I. The quartz at stage II is massive, coexisting with feldspar and muscovite, and usually 2–5 cm in size (Fig. 2D).
Fig. 1 Distribution map of the Zhawulong deposit area (modified from Li et al., 2018).

Fig. 2 Photographs of an albite–spodumene pegmatite specimen from the Zhawulong deposit.
(A) and (B) spodumene coexist with albite and quartz; the spodumene has a comb-like structure and is euhedral. (C) spodumene in a granular structure coexists with albite and quartz. (D) late massive coarse-grained quartz II coexists with albite. Spd: spodumene; Qtz: quartz; Ab: albite.
4 Fluid inclusion petrography

In this study, the albite–spodumene belts in albite–spodumene pegmatite veins (veins 97, 100, and 108) are studied systematically. The sampling location is shown in Fig. 1.

Three different fluid inclusion assemblages (FIAs) can be distinguished: crystal-rich fluid inclusions (L+V+S), CO$_2$–NaCl–H$_2$O fluid inclusions (CO$_2$ (G) +CO$_2$ (L) +L), and NaCl–H$_2$O fluid inclusions (L+V).

Crystal-rich fluid inclusions and CO$_2$–NaCl–H$_2$O fluid inclusions are the predominant fluid inclusion populations in the spodumene. The crystal-rich fluid inclusions are distributed as planar clusters on {110} and along fractures (Fig. 3A, B). The sizes of the crystal-rich fluid inclusions vary, up to 60 μm. The solid phase in these fluid inclusions contains euhedral-granular crystals in circular, elliptical, or cubic shapes. The crystals typically occupy less than 20% of the fluid inclusions’ volume, and they are often found at the edges of the fluid inclusions. The fluid portions are mainly two- or three-phase, with the latter containing CO$_2$ as in CO$_2$–NaCl–H$_2$O. The CO$_2$ occupies 60–80 vol%. Although not all inclusions show the same crystal/liquid ratio and CO$_2$ volume percentage, the fluid inclusions containing crystals usually have similar crystal/liquid ratio and CO$_2$ volume percentages in the same inclusion (Fig. 3A, B). In addition, some CO$_2$–NaCl–H$_2$O fluid inclusions of similar shape and size are found to coexist with the crystal-rich fluid inclusions in spodumene (Fig. 3C). They may have formed either by necking down from the crystal-rich fluid inclusions (London et al., 1986; Anderson et al., 2001) or during cooling. They may be due to the absence of obvious crystals since the crystals precipitated on the walls of the fluid inclusions (Li and Chou, 2017). However, due to the large number of isolated primary fluid inclusions of CO$_2$–NaCl–H$_2$O in spodumene at stage II, CO$_2$–NaCl–H$_2$O fluid inclusions are likely to be captured as a primary origin fluid by spodumene at stage II (Fig. 3D, E), which formed later than the crystal-rich fluid inclusions. NaCl–H$_2$O fluid inclusions can be found as secondary origin, usually arranged in long strips along the spodumene fissures (Fig. 3F). The size is roughly between 5 and 15 μm, and the vapor volume is generally between 10% and 30%.

CO$_2$–NaCl–H$_2$O fluid inclusions are found in the quartz at stage I. CO$_2$–NaCl–H$_2$O fluid inclusions are distributed as clusters, mainly in circular or elliptical shapes, presenting primary characteristics (Fig. 3G). The size is generally 6~80 μm. At room temperature (20 °C), the CO$_2$ volume phase is between 10% and 90%, and most of them are more than 50%, with a vapor volume ratio between 10% and 30%. NaCl–H$_2$O inclusions can also occur in the quartz. The NaCl–H$_2$O fluid inclusions in the quartz at stage I are usually distributed, irregularly and distortedly, in an obvious orientation along cracks, presenting secondary characteristics (Fig. 3H). The size of the NaCl–H$_2$O fluid inclusions is mainly 3~5 μm with circular or elliptical shapes, and the vapor volume is generally between 10% and 30%. However, the NaCl–H$_2$O fluid inclusions in the quartz at stage II are usually distributed regularly in nearly circular or elliptical assemblages, presenting the characteristics of primary inclusions. The size of the inclusions is mainly 3~5 μm, and the vapor volume ratio is generally between 10% and 30% (Fig. 3I).

5. Analytical methods

In this study, we selected some representative fluid inclusions from FIAs, with primary characteristics from typical pegmatite veins, in the Zhawulong deposit.

To understand the fluid inclusions’ compositions, laser Raman probe (LRM) analyses were carried out in the Laboratory of the Institute of Mineral Resources of the Chinese Academy of Geological Sciences. An excitation wavelength of 514.5 nm was used, and the laser power at the sample surface was 20 mW. The beam spot diameter was 1 μm, and the scanning range was 100–4500 cm$^{-1}$. The spectrometer was calibrated with silica with an accuracy of ±0.2 cm$^{-1}$. The analysis sample was a double-sided, polished sheet with a thickness of approximately 300 μm.
Fig. 3 Characteristics of fluid inclusions from pegmatite veins in the Zhawulong deposit. (A) and (B) Crystal-rich fluid inclusions assemblages (FIA) have a long, strip-oriented distribution, but the directional fluid inclusions did not cut through the boundary of adjacent minerals, presenting the characteristics of primary origin. Crystal-rich fluid inclusions assemblages had a similar crystal/fluid ratio and CO$_2$ volume ratio. (C) Crystal-rich FIA have a similar crystal/fluid ratio as the CO$_2$–NaCl–H$_2$O fluid inclusions. (D) and (E) CO$_2$–NaCl–H$_2$O fluid inclusions are separately distributed in spodumene II, indicating the characteristics of primary inclusions. (F) Two phases of fluid inclusions occurred in spodumene I: crystal-rich fluid inclusions and CO$_2$–NaCl–H$_2$O fluid inclusions. The CO$_2$–NaCl–H$_2$O fluid inclusions as secondary origin cut the crystal-rich fluid inclusion of primary origin. (G) The CO$_2$–NaCl–H$_2$O fluid inclusions in quartz I are regularly distributed in a circular or elliptical shape, implying primary characteristics. (H) NaCl–H$_2$O fluid inclusions in quartz I are linearly and irregularly arranged along micro-fissures, showing secondary origin. (I) NaCl–H$_2$O fluid inclusions in quartz II are regularly distributed in a round shape, presenting primary characteristics.

The microthermometric data of fluid inclusions were collected by using the Linkam THMS600 heating and freezing stage at the Laboratory of the Institute of Mineral Resources, Chinese Academy of Geological Sciences, which was calibrated at the triple points of H$_2$O (0.0 °C) and CO$_2$ (−56.6 °C), with an estimated accuracy of ±0.1 °C. Salinities for the CO$_2$–NaCl–H$_2$O fluid inclusions were calculated from the final melting temperatures of CO$_2$–clathrate after Collins (1979). Salinities for the NaCl–H$_2$O fluid inclusions were calculated from the final melting temperatures of ice after Bodnar (1993).

6. Results

6.1 Laser Raman Analysis
The vapor, liquid, and crystal phases of fluid inclusions were analyzed with Raman spectroscopy. The results showed the characteristic peaks of cristobalite at 415 cm\(^{-1}\) and zabuyelite (Li\(_2\)CO\(_3\)) at 96, 129, 157, 191, and 1098 cm\(^{-1}\) (Fig. 6 and Fig. 7) (Li and Chou, 2016) after the host mineral spodumene peaks (1075, 1022, 707, 522, 393, 355, 327, and 248 cm\(^{-1}\)) had been excluded. CO\(_2\) was the main gas in the CO\(_2\)–NaCl–H\(_2\)O fluid inclusions. In addition, a small amount of CH\(_4\) (2913–2919 cm\(^{-1}\)) (Fig. 8a, b) was found in the CO\(_2\)–NaCl–H\(_2\)O fluid inclusions. The gas in the NaCl–H\(_2\)O fluid inclusions was mainly H\(_2\)O (3310–3610 cm\(^{-1}\)).

### 6.2 Microthermometric Data

It was very difficult to measure the complete homogenization temperature of the crystal-rich fluid inclusions because they would easily explode during heating. Therefore, only a few data have been measured for this paper, ranging from 500 °C to 580 °C. The homogenization temperature of the crystal-rich fluid inclusions ranges from 308 °C to 420 °C, which is similar to that of the CO\(_2\) to NaCl to H\(_2\)O fluid inclusions. The microthermometric experiments for crystal-rich fluid inclusions containing CO\(_2\) showed that the final melting temperatures were between −57.0 °C and −60.0 °C for solid CO\(_2\), indicating the presence of a small amount of other gases. The CO\(_2\)–clathrate melting temperatures were between 5.3 °C and 9.6 °C, indicating a salinity of 3.0–8.5 wt% NaCl equivalent. The carbonic phase homogenized to the liquid phase between 16.5 °C and 29.4 °C, indicating that the bulk density of CO\(_2\) is close to 0.70 g/cm\(^3\) (Sterner and Bodnar, 1991).

The total homogenization temperature of the CO\(_2\)–NaCl–H\(_2\)O fluid inclusions in the spodumene ranged from 278 °C to 412 °C, mainly concentrated between 300 °C and 400 °C with a peak value of 330 °C (Fig. 4a). The microthermometric experiments for CO\(_2\)–NaCl–H\(_2\)O showed that the final melting temperatures were between 57.0 °C and 61.0 °C for solid CO\(_2\), indicating the presence of a small amount of other gases. The CO\(_2\)–clathrate melting temperatures were between 3 °C and 6.5 °C, indicating a salinity of 6.5–11.9 wt% NaCl equivalent. The carbonic phase homogenized to the liquid phase between 16.5 °C and 29.4 °C (Fig. 5a).

The total homogenization temperature of the CO\(_2\)–NaCl–H\(_2\)O inclusions in quartz I ranged from 287 °C to 419 °C, mainly concentrated between 300 °C and 360 °C with a peak value of 340 °C (Table 1; Fig. 4b). The microthermometric experiments for CO\(_2\)–NaCl–H\(_2\)O in quartz I showed that the final melting temperatures were between 57.0 °C and 61.0 °C for solid CO\(_2\), indicating the presence of a small amount of other gases. The CO\(_2\)–clathrate melting temperatures were between 4.7 °C and 7.4 °C, indicating a salinity of 3.3–9.4 wt% NaCl equivalent. The carbonic phase homogenized to the liquid phase between 15.3 °C and 28.4 °C (Fig. 5b).

In quartz II, the homogenization temperature ranged from 203 °C to 302 °C, mainly concentrated between 200 °C and 260 °C with a peak value of 260 °C and the salinity ranged from 2.7 to 13.9 wt% NaCl equivalent (Fig. 5c; Table 1); the density was 0.83–1.05 g/cm\(^3\).

### Table 1 Microthermometric data of fluid inclusions from Zhawulong lithium deposit

<table>
<thead>
<tr>
<th>Minerals</th>
<th>FI</th>
<th>Pegmatite</th>
<th>N</th>
<th>T(_{m, \text{CO}_2})</th>
<th>T(_{m, \text{clath}})</th>
<th>T(_{m, \text{CO}_2, \text{clath}})</th>
<th>T(_{m, \text{ice}})</th>
<th>T(_{m, \text{TOT}})</th>
<th>Salinity</th>
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<tr>
<td>Cristal-rich</td>
<td>No.97</td>
<td>5</td>
<td>5.3–9.6</td>
<td>16.5–29.4</td>
<td>500–580</td>
<td>3.0–8.5</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>No.108</td>
<td>12</td>
<td>-57.0–60.0</td>
<td>5.3–9.6</td>
<td>16.5–29.4</td>
<td>500–600</td>
<td>0.8–8.5</td>
<td></td>
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<tr>
<td>CO(_2)-NaCl-H(_2)O</td>
<td>No.97</td>
<td>57</td>
<td>3–5.9</td>
<td>16.5–29.4</td>
<td>309–412</td>
<td>7.5–11.9</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>No.100</td>
<td>15</td>
<td>-57.0–60.3</td>
<td>3–5.9</td>
<td>16.5–29.4</td>
<td>292–402</td>
<td>6.5–10.9</td>
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<tr>
<td></td>
<td>No.108</td>
<td>42</td>
<td>-57.3–61.0</td>
<td>3–5.9</td>
<td>16.5–29.4</td>
<td>278–405</td>
<td>7.2–10.2</td>
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<tr>
<td>CO(_2)-NaCl-H(_2)O</td>
<td>No.97</td>
<td>39</td>
<td>4.2–6.1</td>
<td>17.1–26.5</td>
<td>287–419</td>
<td>5.9–9.4</td>
<td></td>
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<tr>
<td></td>
<td>No.100</td>
<td>27</td>
<td>-57.0–60.0</td>
<td>4.2–6.1</td>
<td>15.8–28.4</td>
<td>294–419</td>
<td>5.9–9.4</td>
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<td>No.108</td>
<td>45</td>
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<td>4.2–6.1</td>
<td>15.8–28.4</td>
<td>294–412</td>
<td>4.4–9.6</td>
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<td>quartz</td>
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<td>-10.0–1.6</td>
<td>232–298</td>
<td>2.7–13.9</td>
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<td>NaCl-H(_2)O</td>
<td>No.100</td>
<td>78</td>
<td>-9.1–2.0</td>
<td>203–293</td>
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<td></td>
<td>No.108</td>
<td>62</td>
<td>-9.8–2.0</td>
<td>212–302</td>
<td>3.4–13.8</td>
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Abbreviations: FI=fluid inclusion, N=number of significant values, T\(_m, \text{CO}_2\): final melting temperature of solid CO\(_2\); T\(_m, \text{clath}\): final melting temperature of CO\(_2\)-H\(_2\)O clathrate (°C); T\(_m, \text{CO}_2, \text{clath}\): homogenization temperature of the CO\(_2\) phases (°C); T\(_m, \text{ice}\): final melting temperature of ice (°C); T\(_m, \text{TOT}\): total homogenization temperature of fluid inclusions (°C); the unit of salinity is wt% NaCl equivalent.
Fig. 4 Histogram of homogenization temperatures of NaCl–H2O and CO2–NaCl–H2O fluid inclusions from different albite pegmatites veins in the Zhawulong deposit.

(A) CO2–NaCl–H2O fluid inclusions of spodumene II. (B) CO2–NaCl–H2O fluid inclusions of quartz I. (C) NaCl–H2O fluid inclusions of quartz II.
Fig. 5 Histogram of salinity of NaCl–H$_2$O and CO$_2$–NaCl–H$_2$O fluid inclusions from different albite pegmatite veins in the Zhawulong deposit. (A) CO$_2$–NaCl–H$_2$O fluid inclusions of spodumene II. (B) CO$_2$–NaCl–H$_2$O fluid inclusions of quartz. (C) NaCl–H$_2$O fluid inclusions of quartz II.
Fig. 6 Laser Raman spectra of fluid inclusions from pegmatite veins in the Zhawulong deposit.

Fig. 7 The crystal-rich inclusions hosted in spodumene from the Zhawulong deposit, Crt: cristobalite; Zab: Zabulite (Li₂CO₃); Aq: liquid phase.

Fig. 8 Laser Raman spectra of fluid inclusions in quartz (Qtz) from pegmatite veins in the Zhawulong deposit.

7 Discussion

7.1 Fluid inclusion characteristics

Previous studies have suggested that daughter minerals, crystallized from the fluids rather than
trapped accidently, can reflect fluid properties. The early fluids were mainly trapped as crystal-rich fluid in the spodumene of the albite–spodumene pegmatite from the Zhawulong deposit. The following features indicate that crystal-rich fluid inclusions remain closed after their entrapment, and these crystals were not accidentally trapped but are actually daughter minerals: (1) the crystal-rich fluid inclusions have a uniform crystal/fluid proportion, and their total homogenization melting temperatures (400 °C to 600 °C) were similar; (2) zabuyelite and cristobalite only occurred in the solid phase of fluid inclusions and were absent from the pegmatite veins’ minerals; and (3) the crystals are euhedral and have similar grain sizes, indicating a system that was rich in H2O during crystallization after capture (Li and Chou, 2017).

Crystal-rich fluid inclusions occur widely in rare granite pegmatite deposits, such as the Jiajika lithium deposits (Li et al., 2006; Li and Chou, 2016), the Keeruyi lithium deposits in Western Sichuan (Li et al., 2007), the No. 3 pegmatite lithium deposits in Koktokay and Xinjiang (Lu et al., 1996; Zhu et al., 2000), and the Tanco lithium-beryllium deposits in Canada (Anderson et al., 2001). These inclusions may represent a kind of volatile-rich pegmatite fluid or melt which was captured at the pegmatite melt-fluid transition stage by the differentiation of granitic magma (London, 1986, 2018; Thomas et al., 2000; Li et al., 2006). According to the microthermometric analyses, the fluid or melt of pegmatite in the Zhawulong deposit showed characteristics of a low salinity fluid, like other pegmatite lithium deposits (Foord, 1976; Taylor et al., 1979; London, 1986; Li et al., 2016; 2017). It may be because Li+ mainly occurred not with Cl− but with CO3 2− (Li2CO3, Zabuyelite) in the ore-forming fluids (Anderson, 2001; Zhou, 2013; Li and Chou, 2013, 2016). Therefore, the pegmatite fluid (melt) in the Zhawulong deposit was formed under high temperature and low salinity conditions enriched in volatiles (CO2 and CH4), alkali metal elements (Na, Li, etc.), and carbonate.

Both crystal-rich fluid inclusions and CO2–NaCl–H2O inclusions were preserved in spodumene I. CO2–NaCl–H2O fluid inclusions, as secondary fluids, cut crystal-rich fluid inclusions as the primary fluid in spodumene I. Crystal-rich fluid inclusions formed at a higher temperature (more than 500 °C) than CO2–NaCl–H2O fluid inclusions (278 °C to 419 °C). However, they shared the same homogenization temperature and composition in the fluid phase. This indicated that the CO2–NaCl–H2O fluid might be the product of CO2 differentiation after saturation in the crystal-rich fluid. Therefore, we propose the crystal-rich fluid inclusions represent the pegmatite-forming fluids, whereas the CO2–NaCl–H2O fluid inclusions post-date the crystal-rich fluid inclusions as the post-pegmatite fluids. In summary, the CO2–NaCl–H2O represents the hydrothermal stage, showing medium-high temperature (278 °C to 419 °C), low salinity (4.4–11.9 wt.% NaCl equivalent), and volatile-rich components (CO2 and CH4).

The NaCl–H2O fluid inclusions were hosted in quartz II. The total homogenization temperature ranged from 203 °C to 302 °C, and salinity ranged from 2.7 to 13.9 wt.% NaCl equivalent. The fluids at this stage are characterized by low temperature, low salinity, and a relatively simple composition.

7.2 Physicochemical conditions of pegmatite crystallization

The capture conditions of the crystal-rich fluid inclusions represent the physical and chemical conditions of the pegmatite-forming melt or fluid. The crystal-rich fluid inclusions contained various kinds of crystals, indicating that at least one component was saturated during the capturing process. Once the fluid was captured, the components would have separated and precipitated immediately (London, 2008). The original melt or fluid in pegmatite underwent magmatic differentiation to form the zoning and coarse minerals of the pegmatite veins in the Zhawulong deposit at the early stage. Subsequently, lithium migrated and became enriched when the pegmatite melt or fluid separated from the granitic magma. The homogenization temperature of such an inclusion can also be regarded as its capture temperature. According to the microthermometric data (Table 1), the crystal-rich fluid inclusions were formed under salinity of 6 wt.% NaCl equivalent, CO2 occupation of 60–80 vol.%, density of 0.8 g/cm3 and temperature of 500 °C to 580 °C. By combining the PVT phase diagram of a CO2–NaCl–H2O system with the microthermometric data of this study (Fig. 9) (Brown and Lamb, 1989), the minimum pressure range for capturing the crystal-rich fluid inclusions can be limited to 310–480 MPa (average is 350 MPa). The 350 MPa value was used to approximate the capture pressure (Fig. 10; range A).
The homogenization temperature of the CO₂–NaCl–H₂O fluid inclusions is equal to their capture temperature (Li et al., 2008). According to the microthermometric data, the CO₂–NaCl–H₂O fluid corresponds to the isochore with salinity of 8 wt.% NaCl equivalent, CO₂ filling degree of 70~80%, and density of 0.8 g/cm³ (Fig. 10; Brown and Lamb, 1989). The capture temperature of the CO₂–NaCl–H₂O fluid in spodumene I (350~400 °C) is slightly higher than that in quartz I. As a result, the isochore and capture temperature of the CO₂–NaCl–H₂O fluid inclusions (300~400 °C) limit the ranges of B and C in Fig. 10 (Brown and Lamb, 1989), representing the lower limits of capture pressure for the CO₂–NaCl–H₂O fluids in spodumene I and quartz I, respectively.

According to the homogeneous temperature data, the NaCl–H₂O fluid corresponds to the isochore of 10 wt.% NaCl equivalent (Fig. 10; Roedder and Bodnar, 1980). Because nepheline and petalite are not found in the Zhaowulong deposit, the boundaries of “spodumene + quartz / petalite + quartz” and “eucryptite + quartz / spodumene” delimit the NaCl–H₂O fluid’s physical and chemical conditions. The pressure range C of the CO₂–NaCl–H₂O fluid inclusions is the upper limit of the NaCl–H₂O fluid inclusions’ physical and chemical conditions. By considering these restrictions mentioned above, the pressure range D constrains the lower limit of capture pressure for the NaCl–H₂O fluid inclusions hosted in quartz (Fig. 10; Roedder and Bodnar, 1980).

![Fig. 9 Emplacement pressures estimated from the P–T conditions of crystal-rich inclusions (modified from Brown, 1989).](image)

According to the homogenization temperature data of Zhaowulong and the PVT phase diagram (Brown and Lamb, 1989) of the CO₂–NaCl–H₂O system with crystal-rich fluid inclusions, the inclusions correspond to a CO₂ density of 0.8 g/cm³ and a salinity of 6 wt.% NaCl equivalent. The lower limit of ore-forming pressure was 310~480 MPa with CO₂ filling degree of 60~80 vol.% and temperature of 500~580 °C.

The evolution of ore-forming fluids in the Zhaowulong deposit can be described as follows (Fig. 10):

Pegmatite fluids or melts were separated from granite at approximately 550~700 °C (Fig. 10). At the early stage of the pegmatite fluid or melt (Fig. 10; range A), the P–T condition was close to, or at the boundary of, the “lithium–feldspar–spodumene–quartz” phase at 500~600 °C and 350 MPa, and the fluid was rich in water and boron-rich silicate and contained a small amount of CO₂. Moreover, the pegmatite melt or fluid was saturated with the components of quartz, albite, and many other kinds of crystals. At this stage, the pegmatite melts or fluids, which were formed by differentiation and separation from granitic magma, occurred simultaneously with crystallization of spodumene in the pegmatite. This phenomenon is common in other typical pegmatite lithium deposits, such as the No. 3 pegmatite lithium deposit in Xinjiang (Lu et al., 1996) and the Tanco pegmatite Li-Be deposit in
Canada (London, 1986). At approximately 400 °C (Fig. 10; range B, C), the CO₂–NaCl–H₂O fluid inclusions formed after the formation of the crystal-rich fluid inclusions. The CO₂–NaCl–H₂O fluid inclusions were the product of crystal-rich fluid inclusions (pegmatite melt or fluid) by CO₂ differentiation after saturation (Fig. 10; range B, C), which represented the boundary between the magmatic–hydrothermal transition stage and the hydrothermal stage. At approximately 400–500 °C, boron-rich fluids precipitated into tourmaline, albite, muscovite (lepidolite), quartz and ore minerals (such as spodumene). Next, the ore-forming fluids evolved into relatively low-density and low-salinity brine solutions. The phase separated from the CO₂–NaCl–H₂O fluids into the NaCl–H₂O fluids at approximately 300 °C (Fig. 10; range D).

Fig. 10 Physiochemical conditions of the formation of pegmatites in the Zhawulong (modified from London et al., 1984).

The gray area A–D in the figure represents the capture conditions of different fluids. Range A is the capture conditions of crystal-rich fluid inclusions; range B is the capture conditions of CO₂–NaCl–H₂O fluid inclusions in spodumene I; range C is the capture conditions of CO₂–NaCl–H₂O fluid inclusions in quartz I; and range D is the capture conditions of NaCl–H₂O fluid inclusions in quartz II. The red dotted line is the CO₂–NaCl–H₂O isochore with salinity of 6 wt.% NaCl equivalent, CO₂ filling degree of 60–80 vol.%, and density of 0.70 g/cm³. The black dotted line is the CO₂–NaCl–H₂O isochore with salinity of 8 wt.% NaCl equivalent, CO₂ filling degree of 60–80 vol.%, and density of 0.70 g/cm³. The blue thin line is the NaCl–H₂O isochore with salinity of 10 wt.% equivalent and temperature of 200–260 °C.

7.3 Comparison with typical lithium deposits in China

The ore-forming fluids of granitic pegmatite rare metal deposits are usually rich in volatile components (CO₂, H₂O, F, and B) and rare metal elements (Li, Rb, Cs, Be, Ta, Nb, Sn, and W) (Li et al., 2008). Petrology experiments have shown that volatile components play an important role in forming
granite pegmatite rare metal deposits (Keppler, 1993; Thomas et al., 2005; Zhang et al., 2005). Volatile components can easily form various complexes or compounds with rare metals and could help with migration and enrichment of these metallogenic elements (Audétat and Keppler, 2004; Li et al., 2000). During the crystallization and differentiation process, volatile-rich melts have a strong capacity to concentrate lithium in pegmatite deposits like the Jiajika and Zhawulong deposits. Consequently, the contents of rare metals in the melt phase are increased by several orders of magnitude (Xiong et al., 1998; Zhu et al., 2002; Jackson et al., 1989; Thomas et al., 2011c) and further enriched to form spodumene (Xiong et al., 1998; Zhu et al., 2002; Jackson and Helgeson, 1985; Keppler and Wyllie, 1991).

The ore-forming fluids in the Zhawulong deposit share some features with the famous pegmatite lithium deposits as follows (e.g., London, 1986, 2018; Lu et al., 1996; Thomas et al., 2005, 2016; Li et al., 2007; Li and Chou, 2016, 2017): (1) the same types of fluid inclusions, namely, crystal-rich fluid inclusions, CO₂–NaCl–H₂O fluid inclusions, and NaCl–H₂O fluid inclusion; (2) almost the same daughter minerals, such as albite, quartz, and zabuyelite; and (3) similar volatile-rich components (H₂O, CH₄, and CO₂). However, the P–T conditions in the Zhawulong deposit (Fig. 11; Table 2) were similar to the typical lithium deposits in China, but remarkably different from the Tanco deposit (Fig. 11; Table 2). This might be because petalite has not yet been found in the Zhawulong and other deposits in China, and the P–T history only evolved in the field of “spodumene-spodumene+2quartz” of the phase diagram.

Fig.11 Physiochemical conditions of different pegmatites from Jiajika (Li and Chou, 2016), Zhawulong, Koktokay, and Tanco (modified after London, 1986). Among them, the lines of different colors represent P–T evolutionary tracers of the Jiajika (yellow) (Li and Chou, 2016), Zhawulong (red) and Koktokay (blue) (Lu et al., 1996), and Tanco (gray) (London, 1986) deposits.
### Table 2  part of the metallogenic temperature in pegmatite lithium deposit

<table>
<thead>
<tr>
<th>Deposits</th>
<th>Host mineral</th>
<th>types</th>
<th>$T_{h, CO_2}$</th>
<th>$T_{h, TOT}$</th>
<th>$T_{m, clath}$</th>
<th>$T_{m, ice}$</th>
<th>Salinity</th>
<th>Reference</th>
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<td>Zhaowulong</td>
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<td>Crystal-rich</td>
<td>16.5–29.4</td>
<td>≥500</td>
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<td>0.8–8.5</td>
<td></td>
<td>this work</td>
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<td></td>
<td>CO$_2$-NaCl-H$_2$O</td>
<td>16.5–29.4</td>
<td>278–412</td>
<td>3–6.5</td>
<td>6.6–11.9</td>
<td></td>
<td>Li and Chou, 2016; 2017</td>
</tr>
<tr>
<td></td>
<td></td>
<td>quartz</td>
<td>15.3–28.4</td>
<td>287–419</td>
<td>4.1–7.4</td>
<td>4.4–9.6</td>
<td></td>
<td>Li et al., 2007</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NaCl-H$_2$O</td>
<td>203–302</td>
<td>16.5–29.4</td>
<td>2.7–13.9</td>
<td></td>
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<td>Li et al., 2007</td>
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<tr>
<td></td>
<td>quartz</td>
<td></td>
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<td>203–302</td>
<td>16.5–29.4</td>
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<td>Li et al., 2007</td>
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<td></td>
<td>NaCl-H$_2$O</td>
<td>250–400</td>
<td>0–10</td>
<td>7</td>
<td></td>
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<td>Li et al., 2015</td>
</tr>
<tr>
<td>No.134 pegmatite in Jiajika</td>
<td>Spodumene</td>
<td>Crystal-rich</td>
<td>26–28</td>
<td>500–720</td>
<td>0–10</td>
<td>6</td>
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<td>Li and Chou, 2016; 2017</td>
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<td>CO$_2$-NaCl-H$_2$O</td>
<td>26–28</td>
<td>246–415</td>
<td>3.5–8.2</td>
<td>3.7–10.8</td>
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<td>190–376</td>
<td>19.3–28.0</td>
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<td>250–400</td>
<td>0–10</td>
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<td>Li et al., 2007</td>
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<td></td>
<td>quartz</td>
<td></td>
<td></td>
<td>720–830</td>
<td>310–360</td>
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<td></td>
<td>London, 1986; Anderson et al., 2001</td>
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<td>NaCl-H$_2$O</td>
<td>190–376</td>
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<td>London, 1986; Anderson et al., 2001</td>
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</table>
8 Conclusion

(1) The evolutionary process of pegmatite in the Zhawulong deposit can be classified into three stages from early to late: (1) crystal-rich fluids in high temperature, low salinity, silicate-rich, alkali-rich, and volatile-rich conditions; (2) CO$_2$-NaCl-H$_2$O fluids in medium-high temperature and low salinity conditions; and (3) NaCl-H$_2$O fluids in low temperature and low salinity conditions.

(2) The P-T condition suggests that spodumene I crystallized at the early stage of about 480 MPa and 600 °C, and then spodumene II and quartz I crystallized during decreasing in temperature and pressure. The crystallization of quartz was predominant till 200 MPa and 300 °C. The crystallization conditions of pegmatite veins in Zhawulong deposit were mainly confined to “spodumene-spodumene+2quartz” stable area.

(3) The temperatures and pressure conditions of the ore-forming fluids from the Zhawulong deposit are similar to those of the Jiajika deposit in the Songfan-Ganzi metallogenic belt. The ore-forming fluids in the Zhawulong deposit not only have sufficient materials to crystallize rare metal minerals, such as spodumene, but also have proper temperature and pressure conditions to ensure the growth of spodumene. The Zhawulong deposit has good ore-forming conditions and prospecting potential.

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