Ore-forming Fluid and Metallogenic Mechanism of Wolframite–Quartz Vein-type Tungsten Deposits in South China

NI Pei*, LI Wensheng and PAN Junyi

State Key Laboratory for Mineral Deposits Research, Institute of Geo-Fluids, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210023, China

Abstract: South China is endowed with copious wolframite–quartz vein-type W deposits that provide a significant contribution to the world’s tungsten production. Mineralization is spatially associated with highly evolved granites, which have been interpreted as products of ancient crustal anatexis. Ore veins are mainly hosted in low-grade metamorphosed quartz sandstone, slate and granitic rocks. The ore minerals mainly comprise wolframite, cassiterite, scheelite and pyrite, with minor molybdenite, arsenopyrite and chalcopyrite. Typical steeply dipping veins can be divided into five zones from top to bottom, namely: (I) thread, (II) veinlet, (III) moderate vein, (IV) thick vein, and (V) thin out zones. In general, three types of fluid inclusions at room temperature are commonly recognized in wolframite and/or quartz from these veins: two-phase liquid-rich (type L), two-phase CO₂-bearing (type CB), and CO₂-rich (type C). Comparative microthermometry performed on fluid inclusions hosted in wolframite and associated quartz indicates that most wolframite was not co-precipitated with the coexisting quartz. Detailed petrographic observation and cathodoluminescence (CL) imaging on coexisting wolframite and quartz of the Yaogangxian deposit, show repeated precipitation of quartz, wolframite, and muscovite, suggesting a more complex fluid process forming these veins. Previous studies of H-O isotopes and fluid inclusions suggested that the main ore-forming fluids forming the wolframite–quartz vein-type deposits had a magmatic source, whereas an unresolved debate is centered on whether mantle material supplemented the ore-forming fluids. The variable CO₂ contents in the ore-forming fluids also implies that CO₂ might have had a positive effect on ore formation. Fluid inclusion studies indicate that wolframite was most likely deposited during cooling from an initial H₂O + NaCl ± CO₂ magmatic fluid. In addition, fluid-phase separation and/or mixing with sedimentary fluid might also have played an important role in promoting wolframite deposition. We speculate that these processes determine the precipitation of W to varying degrees whereas the leading mechanistic cause remains an open question. Comprehensive studies on spatial variation of fluid inclusions show that both the steeply and gently dipping veins are consistent with the “five floors” model that may have broader applications to exploration of wolframite–quartz vein-type deposits. Recent quantitative analysis of wolframite- and quartz-hosted fluid inclusions by laser ablation inductively-coupled plasma mass spectrometry shows enhanced advantages in revealing fluid evolution, tracing the fluid source and dissecting the ore precipitation process. Further studies on wolframite–quartz vein-type W deposits to bring a deeper understanding on ore-forming fluids and the metallogenic mechanism involved.

Key words: metallogeny, wolframite-quartz vein, fluid inclusions, microthermometry, Nanling region

1 Introduction

Tungsten (W) deposits in China contribute more than 58% of the world’s tungsten resources (U.S. Geological Survey, 2018). Many world-class and large-scale tungsten deposits have been exposed in China, especially in the South China Block (SCB) (Hsu, 1943; Lu, 1986; Hua et al., 2005; Mao et al., 2007; Chen et al., 2008; Hu and Zhou, 2012; Chen et al., 2013; Ni et al., 2015; Yuan et al., 2018) (Fig. 1). According to the mineralization characteristics, W deposits in South China are generally divided into pegmatite-, wolframite–quartz vein-, scheelite–quartz vein-, scheelite-bearing skarn-, wolframite-bearing greisen-, and porphyry types (Hsu, 1943; Lu, 1986; Harlaux et al., 2018). Although several large to super-large granite-related porphyry and skarn W polymetallic deposits, such as Dahutang W–Mo, Zhuxi W–Cu–Mo, and Yangchuling W–Mo, have been discovered and exploited recently in South China (Mao et al., 2017; Feng et al., 2018), the wolframite–quartz vein-type W deposit has the longest mining history and the highest industrial value (Lu, 1986; Ni et al., 2015; Zhao et al., 2017). Typical examples for wolframite–quartz vein-type W deposits include Xihuashan, Piaotang, Yaogangxian, Pangushan, Dajishan, Meiziwo and Maoping (Fig. 1).

Wolframite–quartz vein type W deposits, generally related to granitic intrusions, play a significant role in both

* Corresponding author. E-mail: peini@nju.edu.cn

© 2020 Geological Society of China
China’s and global W production (Hsu, 1943; Tanelli, 1982; Tan, 1985; Lu, 1986; Liu and Ma, 1993; Hua et al., 2005; Mao et al., 2007; Hu and Zhou, 2012). Discovery of south China wolframite–quartz vein type W deposits began with the Xihuashan deposit in 1907, followed by the Yaogangxian deposit in 1911. Systematic description of wolframite–quartz vein-type W deposits can be traced back to the beginning of the 20th century (Irving, 1903; Lindgren, 1907; Hess, 1908).

Early studies on the metallogenic mechanisms of such deposits were mostly limited to qualitative description. Since Roedder (1960) first applied the fluid-inclusion method to the study of ore deposits, fluid inclusion has gradually become indispensable to the study of the metallogenic mechanism (Roedder, 1984; Fan et al., 2003; Rusk et al., 2008; Su et al., 2009; Bodnar et al., 2014; Ni et al., 2015). A significant amount of fluid-inclusion studies on wolframite–quartz vein-type W deposits have been conducted since the 1970s, including those in Bolivia (Landis and Rye, 1974), Russia (Naumov and Ivanova, 1971; Pokrovski and Purkov, 1975; Kozłowski et al., 1975), Portugal (Noronha, 1974; Kelly and Rye, 1979), Britain (Jackson and Rankin, 1976; Shepherd et al., 1976), Japan (Enjoji, 1976), and Canada (Higgins, 1980). At the same time, there have been few fluid-inclusion researches on the deposits in South China (Zeng and Yang, 1975; Lu et al., 1977; Li, 1981). It is noteworthy that these fluid-inclusion studies focused mainly on inclusions that were hosted by quartz and other gangue minerals coexisting with wolframite. Since the 1980s, the invention of infrared microscopy provided a window for investigating the internal structure and fluid inclusions in opaque ore minerals (Campbell et al., 1984). Subsequently, a series of research works have been carried out on wolframite-hosted fluid inclusions used to directly characterize the ore-forming fluids (Campbell and Robinson, 1987; Campbell and Panter, 1990; Lueders, 1996; Rios et al., 2003; Wei et al., 2012; Ni et al., 2015; Chen et al., 2018; Li et al., 2018; Peng et al., 2018; Pan et al., 2019; Peng et al., 2020). In recent years, the application of LA-ICP-MS
analysis of single fluid inclusions (Günther et al., 1998; Heinrich et al., 2003) has provided a new perspective for the study of ore-forming fluids and metallogenic mechanisms (e.g., Audétat et al., 1998; Ulrich et al., 1999; Heinrich et al., 2004; Wilkinson et al., 2009; Su et al., 2009; Large et al., 2016). Lately, this method has been successfully applied to the study of the metallogenic mechanism of wolframite-quartz vein-type W deposits (Lecumberri-Sanchez et al., 2017; Legros et al., 2019; Pan et al., 2019).

Despite decades of research, the nature of the magmatic-hydrothermal system that formed the wolframite-quartz veins remains controversial, and several main aspects include: (1) the fluid processes in quartz and coexisting wolframite (Campbell and Robinson, 1987; Ni et al., 2015; Chen et al., 2018; Korges et al., 2018; Li et al., 2018b; Pan et al., 2019); (2) the source of the ore-forming fluids (Stuart et al., 1995; Polya et al., 2000; Burnard and Polya, 2004; Wang et al., 2009; Hu et al., 2012; Zhai et al., 2012); (3) the role of CO$_2$ in W mineralization (Higgins, 1980, 1985; Wood and Samson, 2000; Ni et al., 2015; Li et al., 2018a; Pan et al., 2019) and (4) the wolframite precipitation mechanism (Heinrich, 1990; So and Yun, 1994; Ni et al., 2015; Lecumberri-Sanchez et al., 2017; Korges et al., 2018; Legros et al., 2019; Pan et al., 2019). In the past decade, we have carried out comprehensive studies on several typical wolframite-quartz vein-type W deposits, such as Maoping, Dajishan, Piaotang, Yaogangxian, Dangping and Pangushan. Based on these results, this paper summarizes the published geology, geochemistry, fluid-inclusion and isotope data from these W deposits mainly in South China and aims to provide a preliminary review of these issues.

### 2 Geological Settings

The SCB was formed by the assembly of the Cathaysia and Yangtze blocks along the intervening Neoproterozoic Jiangnan Orogen (Li et al., 2009; Wang et al., 2014; Yao et al., 2019). Paleoproterozoic to Mesoproterozoic basement outcrops in the Cathaysian Block include the Badu, Chencai and Baoban complexes (Yu et al., 2007). The Yangtze Block consists of minor Archean–Paleoproterozoic crystalline basement, which was unconformably overlain by weakly metamorphosed early Neoproterozoic strata and non-metamorphosed Sinian sedimentary rocks (Yang et al., 2020). The Neoproterozoic basement in the Jiangnan Orogen predominantly consists of the Shuangjiaoshan Group, which mainly comprises phyllite and meta-volcanoclastic rocks (Zhao et al., 2011). The basement is generally overlain by Silurian to Early Triassic marine clastic and carbonate rocks, and Middle Triassic to Early Jurassic paralic clastic rocks (Mao et al., 2017).

A 1300-km wide intracontinental igneous belt is distributed in the whole Cathaysian Block and the eastern part of the Yangtze Block, forming a unique igneous province (Li et al., 2007) (Fig. 1). The emplacement of granitic intrusions occurred intermittently from the Caledonian, and during the Indosinian to Yanshanian, forming voluminous I-, S-, and A-types granitic rocks (Zhou et al., 2006; Li et al., 2020). Voluminous Indosinian granitic plutons are widely distributed in Hunan, Jiangxi, and Guangxi provinces, with a wide range from 260–200 Ma (Chen and Jahn, 1998). Yanshanian magmatism represents the most important tectono-magmatic period in the SCB. Early Yanshanian granitic plutons are widespread in the Nanling and adjacent regions, the emplacement of which is predominantly during 180–142 Ma (Zhou et al., 2006). Late Yanshanian magmatism occurred mainly from 142–67 Ma, forming volcano-subvolcanic intrusion assemblages genetically associated with active continental margin magmatism (Fig. 2b).

With the extensive active input of granitic magma in South China, a unique polymetallic metallogenic province was formed, especially with W–Sn in the Late Jurassic. In Nanling and adjacent regions, wolframite–quartz vein-type and skarn-type W deposits are well developed (Hsu, 1943; Mao et al., 2013; Ni et al., 2015; Zhao et al., 2017; Chiang et al., 2018; Wang et al., 2019) (Fig. 2). Wolframite–quartz vein-type W deposits are particularly well developed in southern Jiangxi Province and northern Guangdong Province, where clastic rocks are widespread. In 1966, a genetic model called the ‘five-floor’ regarding W-bearing quartz veins has been proposed by geologists of No. 932 Team, Guangdong Metallurgical Geological Exploration Corp. (Liu and Ma, 1993) (Fig. 3). The uppermost thread zone (I) usually occurs as the distal end of the deposit and consists of thin quartz and muscovite–dominated veins of < 1 cm in thickness. Ore veins from zone II are commonly 1–5 cm thick and generally consist of wolframite, cassiterite and minor sulfides such as pyrite and chalcopyrite; they have limited economic value (Fig. 3). Zone III is characterized by a complicated ore mineralogy including wolframite, scheelite, cassiterite and various sulfides such as pyrite, chalcopyrite, galena and sphalerite. These ore-bearing veins become less dense but much thicker forming the thick–vein zone (IV) and the lowermost thin-out zone (V) gradually shrinks downwards and becomes much less valuable or nearly barren (Fig. 3). The ‘five-floor’ model applies to a deposit dominated by steeply dipping veins such as at Meiziwo and Yaogangxian (Li et al., 2018b). Recently, Chen et al. (2018) suggested that the ‘five-floor vertical zonation’ model could also be applied to practical exploration for a gently dipping vein orebody. Based on the discovery of disseminated orebodies in granite, a new exploration model, called the “Five Levels + Basement”, was reported (Xu et al., 2008; Wang et al., 2010a; Wang et al., 2019). Both of these models likely represent the concrete expression of the spatial evolutionary process of the ore-bearing hydrothermal fluid.

A large number of geochronological datasets and geological observations obtained during the past decade suggest that the wolframite–quartz vein-type deposit is typically associated with granites and frequently distributed near the contact zone between granitoid and wall-rock (Mao et al., 2007; Hua et al., 2013; Romer and Kroner, 2016; Zhang et al., 2017; Li et al., 2020). High-precision geochronological study shows that wolframite–quartz veins and related granites were mainly formed in the Mesozoic (Yuan et al., 2012; Zhang et al., 2017; Chen
et al., 2019a; Li et al., 2020), although there are a few W deposits formed in the Paleozoic (Chen et al., 2016; Chen et al., 2019b; Zhu et al., 2020). Given the W deposits formed in the Paleozoic were dominated by skarn scheelite, in this paper, we focus on the Mesozoic W metallogenic events (Fig. 4).
Mesozoic wolframite–quartz vein-type W deposits are mainly concentrated in three stages: Triassic, Jurassic and Cretaceous (Fig. 4). According to our statistical results, typical wolframite–quartz vein-type W deposit of Triassic age were predominantly formed in the late Triassic (230–210 Ma) and the total reserves of Triassic wolframite–quartz vein-type W deposits in South China are 289,300 tons (WO$_3$) (Fig. 5a; Table 1). These Triassic W deposits are mainly hosted in the granites, with a small amount in Sinian Metasedimentary rocks (Fig. 5b; Table 1). The Jurassic represents the peak time for the formation of wolframite–quartz vein-type W deposit with total reserves of W reaching 1,588,500 tons (WO$_3$) (160–150 Ma). The host strata mainly include Cambrian metasedimentary and Devonian clastic rocks, represented by major large and super large W deposits such as Xihuashan in Jiangxi province and Yaogangxian in Hunan province (Fig. 5a; Table 1). The Cretaceous W deposits are distributed predominantly in the southwestern margin of the SCB, including the Dajishan W deposit in Guangdong province and the Shanhu W deposit in Guangxi province (Fig. 1). The relative high-grade ore veins of the Cretaceous W deposits occur within Devonian–Triassic metasedimentary rocks. On the basis of previous research, the total reserves of Cretaceous wolframite–quartz vein-type deposits are more than 460,100 tons (WO$_3$) (Fig. 5a; Table 1).

In recent years in South China, great attention has been paid to discovering Indosinian granites and associated W deposits (Fig. 4). Several Triassic–Late Jurassic granitic intrusions and related W deposits have been uncovered in the north of the Nanling region, such as Wufengxian (233 Ma), Dengliuxian (220 Ma, 150 Ma) and Xitian (228 Ma; 152 Ma) (Ma et al., 2005; Chen et al., 2017; Li et al., 2019; Cao et al., 2020). Notably, several Triassic wolframite–quartz vein-type deposits have been reported; for example, molybdenite from wolframite–quartz veins of the Qingshan W deposit in Jiangxi province yielded an Re–Os date of 228.7 ± 2.5 Ma (Zhao et al., 2018). Similarly, the Xiane’tang wolframite–quartz vein-type W deposit yielded a muscovite Ar–Ar date at about 231 Ma (Liu et al., 2008). In the Wangxianling region, wolframite–quartz veins from both the Shuiyuanshan and Yejiwo W deposits show molybdenite Re–Os dates of 220 Ma and 228 Ma, respectively, which are consistent with the zircon U–Pb date for the Triassic Wangxianling pluton (Zhang et al., 2015). In addition, new isotope dating suggests that the late-stage intrusive stocks from the Indosinian Miaoaershan–Yuechengling batholith in western Hunan province are closely associated with W mineralization (Wu et al., 2012; Zhang et al., 2015; Zhu et al., 2020).

The Chuankou W deposit has been studied as a representative locality for quartz-vein deposits in South China.
<table>
<thead>
<tr>
<th>Name</th>
<th>Location</th>
<th>Resource and reserves (10^4t)</th>
<th>Ore mineral</th>
<th>Wall-rock</th>
<th>Granitic intrusion</th>
<th>Age (Ma)</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daijishan</td>
<td>Quannan, Jiangxi</td>
<td>W 16</td>
<td>Wolframite; scheelite</td>
<td>Cambrian metasedimentary</td>
<td>Fine-grained biotite granite</td>
<td>161 ± 1.3</td>
<td>Molybdenite Re-Os</td>
<td>Zhang et al., 2011</td>
</tr>
<tr>
<td>Baxiaimao</td>
<td>Shangyuan, Jiangxi</td>
<td>W 2.9</td>
<td>Wolframite; scheelite</td>
<td>Cambrian metasedimentary</td>
<td>Fine-grained biotite granite</td>
<td>157 ± 1.5</td>
<td>Molybdenite Re-Os</td>
<td>Feng et al., 2012</td>
</tr>
<tr>
<td>Anqiantan</td>
<td>Yudu, Jiangxi</td>
<td>W-Bi</td>
<td>Wolframite; scheelite</td>
<td>Cambrian-Devonian metasedimentary</td>
<td>Fine-grained biotite granite</td>
<td>156.1 ± 3.6</td>
<td>Molybdenite Re-Os</td>
<td>Liu et al., 2010</td>
</tr>
<tr>
<td>Kuimeishan</td>
<td>Dingnan, Jiangxi</td>
<td>W-Bi 5.3</td>
<td>Wolframite; scheelite</td>
<td>Cambrian metasedimentary</td>
<td>Biotite granite</td>
<td>153.7 ± 1.5</td>
<td>Molybdenite Re-Os</td>
<td>Li et al., 2014</td>
</tr>
<tr>
<td>Jiulongbao</td>
<td>Chongyi, Jiangxi</td>
<td>W-Sn 1.9</td>
<td>Wolframite; scheelite</td>
<td>Cambrian metasedimentary</td>
<td>Fine-grained biotite granite</td>
<td>151.5 ± 1.1</td>
<td>Molybdenite Re-Os</td>
<td>Feng et al., 2011</td>
</tr>
<tr>
<td>Zhangdongkeng</td>
<td>Chongyi, Jiangxi</td>
<td>W</td>
<td>Wolframite; scheelite</td>
<td>Cambrian metasedimentary</td>
<td>Fine-grained biotite granite</td>
<td>151.3 ± 1.7</td>
<td>Molybdenite Re-Os</td>
<td>Feng et al., 2011</td>
</tr>
<tr>
<td>Maoping</td>
<td>Chongyi, Jiangxi</td>
<td>W-Mo 10.8</td>
<td>Wolframite; scheelite</td>
<td>Cambrian metasedimentary</td>
<td>Fine-grained biotite granite</td>
<td>156.8 ± 1.5</td>
<td>Cassiterite U-Pb</td>
<td>Chen et al., 2019</td>
</tr>
<tr>
<td>Muziyuan</td>
<td>Chongyi, Jiangxi</td>
<td>W-Sn 0.6</td>
<td>Wolframite; scheelite</td>
<td>Cambrian metasedimentary</td>
<td>Biotite granite</td>
<td>151 ± 8.5</td>
<td>Molybdenite Re-Os</td>
<td>Zhang et al., 2009</td>
</tr>
<tr>
<td>Xushan</td>
<td>Fengcheng, Jiangxi</td>
<td>W</td>
<td>Wolframite</td>
<td>Neoproterozoic</td>
<td>Granite</td>
<td>147.1 ± 3.4</td>
<td>Rb-Sr</td>
<td>Li et al., 2011</td>
</tr>
<tr>
<td>Xingluokeng</td>
<td>Ninghua, Fujian</td>
<td>W</td>
<td>Wolframite; scheelite</td>
<td>Granite</td>
<td>Caled-alkaline granite</td>
<td>156.3 ± 4.8</td>
<td>Molybdenite Re-Os</td>
<td>Zhang et al., 2011</td>
</tr>
<tr>
<td>Niuling</td>
<td>Chongyi, Jiangxi</td>
<td>W-Sn 2.9</td>
<td>Wolframite; scheelite</td>
<td>Cambrian metamorphosed sandstone</td>
<td>Fine-grained biotite granite</td>
<td>152 ± 8.5</td>
<td>Molybdenite Re-Os</td>
<td>Feng et al., 2011</td>
</tr>
<tr>
<td>Panghsuh</td>
<td>Yudu, Jiangxi</td>
<td>W-Bi 11</td>
<td>Wolframite; scheelite</td>
<td>Devonian clastic rocks</td>
<td>Two mica granite</td>
<td>155 ± 2.8</td>
<td>Molybdenite Re-Os</td>
<td>Fang et al., 2014</td>
</tr>
<tr>
<td>Piaoatng</td>
<td>Yudu, Jiangxi</td>
<td>W-Sn 6.9</td>
<td>Wolframite; scheelite</td>
<td>Cambrian metasedimentary</td>
<td>Two mica granite</td>
<td>156 ± 2.8</td>
<td>Cassiterite U-Pb</td>
<td>Zhang et al., 2017</td>
</tr>
<tr>
<td>Taoxikeng</td>
<td>Chongyi, Jiangxi</td>
<td>W-Sn 12.06</td>
<td>Wolframite; scheelite</td>
<td>Paleozoic clastic rocks</td>
<td>Biotite monozonitite</td>
<td>154 ± 3.8</td>
<td>Molybdenite Re-Os</td>
<td>Guo et al., 2011</td>
</tr>
<tr>
<td>Huameiao</td>
<td>Dayu, Jiangxi</td>
<td>W 6.7</td>
<td>Wolframite; scheelite</td>
<td>Cambrian metasedimentary</td>
<td>Fine-grained muscovite granite</td>
<td>158.5 ± 3.8</td>
<td>Molybdenite Re-Os</td>
<td>Yang et al., 2015</td>
</tr>
<tr>
<td>Huangsha</td>
<td>Yudu, Jiangxi</td>
<td>W 12.69</td>
<td>Wolframite; scheelite</td>
<td>Cambrian metasedimentary</td>
<td>Two mica granite</td>
<td>153 ± 3</td>
<td>Molybdenite Re-Os</td>
<td>Wang et al., 2011</td>
</tr>
<tr>
<td>Hukeng</td>
<td>Anfu, Jiangxi</td>
<td>W-Sn 15.4</td>
<td>Wolframite; scheelite</td>
<td>Sinian metasedimentary</td>
<td>Fine-grained muscovite granite</td>
<td>150.2 ± 2.2</td>
<td>Molybdenite Re-Os</td>
<td>Liu et al., 2011</td>
</tr>
<tr>
<td>Xihaoshan</td>
<td>Dayu, Jiangxi</td>
<td>W 20.7</td>
<td>Wolframite; scheelite</td>
<td>Cambrian metasedimentary</td>
<td>Two mica granite</td>
<td>157.8 ± 0.9</td>
<td>Molybdenite Re-Os</td>
<td>Hu et al., 2012</td>
</tr>
<tr>
<td>Zangdong</td>
<td>Dayu, Jiangxi</td>
<td>W 4</td>
<td>Wolframite; scheelite</td>
<td>Cambrian metasedimentary</td>
<td>Fine-grained biotite granite</td>
<td>149.1 ± 7.1</td>
<td>Molybdenite Re-Os</td>
<td>Feng et al., 2011</td>
</tr>
<tr>
<td>Baiyuqian</td>
<td>Rucheng, Hunan</td>
<td>W-Sn 3.3</td>
<td>Wolframite; scheelite</td>
<td>Sinian metasedimentary</td>
<td>Fine-grained biotite granite</td>
<td>169.6 ± 2.7</td>
<td>Molybdenite Re-Os</td>
<td>Wang et al., 2011</td>
</tr>
<tr>
<td>Da’ao</td>
<td>Daoxian, Hunan</td>
<td>W-Sn</td>
<td>Wolframite; scheelite</td>
<td>Sinian metasedimentary</td>
<td>Fine-grained biotite granite</td>
<td>151.3 ± 2.4</td>
<td>Molybdenite Re-Os</td>
<td>Zeng et al., 2007</td>
</tr>
<tr>
<td>Yaogangxian</td>
<td>Chenzhou, Hunan</td>
<td>W 20</td>
<td>Wolframite</td>
<td>Cambrian metasedimentary</td>
<td>Fine-grained biotite granite</td>
<td>158</td>
<td>Cassiterite U-Pb</td>
<td>Li et al., 2020</td>
</tr>
<tr>
<td>Dawangshan</td>
<td>Yibang, Jiangxi</td>
<td>W</td>
<td>Wolframite</td>
<td>Fine-grained biotite granite</td>
<td>Fine-grained biotite granite</td>
<td>147.6 ± 1.8</td>
<td>Molybdenite Re-Os</td>
<td>Yang et al., 2019</td>
</tr>
<tr>
<td>Zhangjialong</td>
<td>Zixing, Hunan</td>
<td>W 5.7</td>
<td>Wolframite</td>
<td>Sinian metasedimentary</td>
<td>Fine-grained biotite granite</td>
<td>160.2 ± 2.2</td>
<td>Molybdenite Re-Os</td>
<td>Yuan et al., 2018</td>
</tr>
<tr>
<td>Zhenkou</td>
<td>Zixing, Hunan</td>
<td>W</td>
<td>Wolframite</td>
<td>Sinian metasedimentary</td>
<td>Fine-grained biotite granite</td>
<td>148.1 ± 0.8</td>
<td>Muscovite Ar-Ar</td>
<td>Yan et al., 2019</td>
</tr>
<tr>
<td>Hejiangkou</td>
<td>Chaling, Hunan</td>
<td>W</td>
<td>Wolframite</td>
<td>Fine-grained granite</td>
<td>Fine-grained biotite granite</td>
<td>156.6 ± 0.7</td>
<td>Muscovite Ar-Ar</td>
<td>Cao et al., 2010</td>
</tr>
<tr>
<td>Gaoling</td>
<td>Dongan, Hunan</td>
<td>W</td>
<td>Wolframite; scheelite</td>
<td>Sinian metasedimentary</td>
<td>Fine-grained biotite granite</td>
<td>212 ± 20</td>
<td>Scheelite Sm-Nd</td>
<td>Zhang et al., 2015</td>
</tr>
<tr>
<td>Qingshan</td>
<td>Chongyi, Jiangxi</td>
<td>W 6</td>
<td>Wolframite; scheelite</td>
<td>Ordovician slate</td>
<td>Medium-grained granite</td>
<td>228.7 ± 2.5</td>
<td>Molybdenite Re-Os</td>
<td>Zhao et al., 2018</td>
</tr>
<tr>
<td>Chaankou</td>
<td>Hengyang, Hunan</td>
<td>W 4.9</td>
<td>Wolframite; scheelite</td>
<td>Sinian metamorphic rocks</td>
<td>Medium-grained granite</td>
<td>212</td>
<td>Wolframite U-Pb</td>
<td>Un</td>
</tr>
<tr>
<td>Xianetang</td>
<td>Chongyi, Jiangxi</td>
<td>W</td>
<td>Wolframite; scheelite</td>
<td>Fine-grained biotite granite</td>
<td>Fine-grained biotite granite</td>
<td>231.4 ± 2.4</td>
<td>Muscovite Ar-Ar</td>
<td>Liu et al., 2010</td>
</tr>
<tr>
<td>Ligurfa</td>
<td>Guanyang, Guangxi</td>
<td>W-Mo 1.13</td>
<td>Wolframite</td>
<td>Fine-grained biotite granite</td>
<td>Fine-grained biotite granite</td>
<td>211.9 ± 6.4</td>
<td>Molybdenite Re-Os</td>
<td>Zou et al., 2009</td>
</tr>
<tr>
<td>Sanjiaowan W</td>
<td>Hengyang, Hunan</td>
<td>W 4.9</td>
<td>Wolframite</td>
<td>Fine-grained biotite granite</td>
<td>Fine-grained biotite granite</td>
<td>225 ± 3.3</td>
<td>Molybdenite Re-Os</td>
<td>Peng et al., 2017</td>
</tr>
<tr>
<td>Shuiyuanshan</td>
<td>Chenzhou, Hunan</td>
<td>W 5</td>
<td>Wolframite</td>
<td>Fine-grained biotite granite</td>
<td>Fine-grained biotite granite</td>
<td>220.7 ± 4.1</td>
<td>Molybdenite Re-Os</td>
<td>Zhang et al., 2015</td>
</tr>
<tr>
<td>Yeqiwo</td>
<td>Chenzhou, Hunan</td>
<td>W 6</td>
<td>Wolframite</td>
<td>Fine-grained biotite granite</td>
<td>Fine-grained biotite granite</td>
<td>228.1 ± 2.6</td>
<td>Molybdenite Re-Os</td>
<td>Zhang et al., 2015</td>
</tr>
</tbody>
</table>
Table 1

<table>
<thead>
<tr>
<th>Name</th>
<th>Location</th>
<th>Resource and reserves (10^4 t)</th>
<th>Ore mineral</th>
<th>Wall-rock</th>
<th>Granitic intrusion</th>
<th>Age (Ma)</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yuntoujie</td>
<td>Ziyuan, Guangxi</td>
<td>W 1</td>
<td>Wolframite</td>
<td>Fine-grained biotite granite</td>
<td>Fine-grained biotite granite</td>
<td>216.8 ± 7.5</td>
<td>Molybdenite Re-Os</td>
<td>Wu et al., 2012</td>
</tr>
<tr>
<td>Meiziwo</td>
<td>Shaoguan, Guangdong</td>
<td>W-Sn</td>
<td>Wolframite; cassiterite</td>
<td>Cambrian-Devonian metasedimentary</td>
<td>Biotite granite</td>
<td>157.7 ± 2.8</td>
<td>Molybdenite Re-Os</td>
<td>Qi et al., 2012</td>
</tr>
<tr>
<td>Hongling</td>
<td>Shaoguan, Guangdong</td>
<td>W</td>
<td>Wolframite; scheelite</td>
<td>Biotite granite</td>
<td>Biotite granite</td>
<td>159.1 ± 1.5</td>
<td>Molybdenite Re-Os</td>
<td>Wang et al., 2010</td>
</tr>
<tr>
<td>Yaoling</td>
<td>Shaoguan, Guangdong</td>
<td>W-Sn</td>
<td>Wolframite; cassiterite</td>
<td>Cambrian-Devonian metasedimentary</td>
<td>Porphyrnic biotite granite</td>
<td>159.5 ± 2.8</td>
<td>Molybdenite Re-Os</td>
<td>Qi et al., 2012</td>
</tr>
<tr>
<td>Shirenzhang</td>
<td>Shaoguan, Guangdong</td>
<td>W 5.3</td>
<td>Wolframite; cassiterite</td>
<td>Devonian metasedimentary</td>
<td>Granite</td>
<td>160 ± 2</td>
<td>Cassiterite U-Pb</td>
<td>Jiang et al., 2018</td>
</tr>
<tr>
<td>Shigushan</td>
<td>Shaoguan, Guangdong</td>
<td>W-Bi</td>
<td>Wolframite; bismuthinite</td>
<td>Cambrian metasedimentary</td>
<td>Granite</td>
<td>154.2 ± 2.7</td>
<td>Molybdenite Re-Os</td>
<td>Fu et al., 2008</td>
</tr>
<tr>
<td>Dongping</td>
<td>Wu’ning, Jiangxi</td>
<td>W 21.4</td>
<td>Wolframite</td>
<td>Neoproterozoic</td>
<td>Granite</td>
<td>132.9 ± 1.4</td>
<td>Zircon U-Pb</td>
<td>Li et al., 2016</td>
</tr>
<tr>
<td>Dajinshan</td>
<td>Yaunfu, Guangdong</td>
<td>W-Sn 5.27</td>
<td>Wolframite; cassiterite</td>
<td>Devonian-Triassic metasedimentary</td>
<td>Porphyrnic biotite granite</td>
<td>84.93 ± 1.42</td>
<td>Molybdenite Re-Os</td>
<td>Yu et al., 2012</td>
</tr>
<tr>
<td>Jubankeng</td>
<td>Shaoguan, Guangdong</td>
<td>W-Sn 12.96</td>
<td>Wolframite; cassiterite</td>
<td>Cambrian-Devonian metasedimentary</td>
<td>Granite</td>
<td>137.7 ± 3.2</td>
<td>Muscovite Ar-Ar</td>
<td>Qi et al., 2012</td>
</tr>
<tr>
<td>Shanhui</td>
<td>Zhongshan, Guangxi</td>
<td>W-Sn 6.38</td>
<td>Wolframite; cassiterite</td>
<td>Cambrian metasedimentary</td>
<td>Granite</td>
<td>100.8 ± 0.7</td>
<td>Muscovite Ar-Ar</td>
<td>Xiao et al., 2011</td>
</tr>
<tr>
<td>Xiangdong</td>
<td>Chaling, Hunan</td>
<td>W</td>
<td>Wolframite</td>
<td>Muscovite granite</td>
<td>Muscovite granite</td>
<td>136.8 ± 3.3</td>
<td>Cassiterite U-Pb</td>
<td>Xiong et al., 2020</td>
</tr>
</tbody>
</table>

Fig. 6. (a) Simplified geological map of the Chuankou W deposit; (b) cross-sections along the main prospecting line in the deposit, showing the spatial relationship between veins and granite; (c) typical wolframite–scheelite quartz vein; (d) wolframite-bearing sample from the Chuankou W deposit.
China (Fig. 6). The quartz-vein system is typically located at the intersection of faults and complex antiformal folds within the regional anticline (Fig. 6a). Recent testing of wolframite U-Pb from a quartz vein provided a date of 212 Ma, which has been interpreted as the time of formation during hydrothermal fluid activity. Two types of W-mineralization quartz veins are exposed in the field: scheelite-bearing quartz veins with a thickness between 2 cm and 20 cm, and wolframite-bearing quartz veins that are at a high angle and that have a thickness of a few centimeters up to 1 meter (Fig. 6c).

Given the above, we suggest that South China has good potential for identification of further Indosinian W mineralization and more attention should be directed to Indosinian W ore prospecting in the region. This requires a better understanding of the timing and tectonic background of the W mineralization and associated granites.

The Jurassic marks one of the most active periods of tectonomagmatism in South China. Widespread intermediate-felsic intrusions were emplaced during this period, especially in the Nanling region. These magmas were emplaced at the intersections between NE- and EW-trending faults and formed a large number of W deposits between 160 Ma to 150 Ma. Many large wolframite-quartz vein-type W deposits such as the Chong-You-Yu and Yushan ore clusters in Jiangxi province, and the Julianshan ore clusters in Guangdong and Jiangxi provinces are associated with 160-Ma high-K calc-alkaline granites, which were derived from ancient crustal material (Li et al., 2020).

Yaogangxian, located in central Nanling region, is a giant W deposit and one of the historic leading W producers in China. Ore-bearing quartz veins are limited...
by a set of NW- to NNW-trending and NWW-trending faults (Fig. 7a). These veins are predominantly hosted by low-grade metasedimentary rocks and the Yanshanian granodiorite (Fig. 8a–b). An early Yanshanian granitic intrusion crops out in an area of an out 1.2 km² to the southeast of Tiane’feng (Fig. 7b). According to the types and geochemical characteristics of these granites, two lithofacies are revealed: one two-mica coarse-grained, and the other muscovite fine-grained. Zircon U-Pb dating of the two granite types shows that magma emplacement occurred at 157–161 Ma (Li et al., 2020).

Individual veins at Yaogangxian are generally approximately 500–1400-m long vertically and show typical vertical zonation (Fig. 7b). Mineralization in the bottom sections of the veins are predominantly silicates and oxides with a large amount of wolframite, whereas sulfides and carbonates increase significantly in the upper parts of the quartz–wolframite veins (Li J K et al., 2018). The main ore minerals include wolframite, scheelite, cassiterite, molybdenite, arsenopyrite, chalcopyrite, and sphalerite. Gangue minerals are mainly quartz, feldspar, fluorite, tourmaline, and muscovite (Fig. 8a). LA-ICP-MS U-Pb dating of hydrothermal cassiterite gives a weighted mean date of 159.5 ± 1.5 Ma and is synchronous with the magma event (Li et al., 2020).

The Maoping deposit is a large W deposit in the Chong-You-Yu ore cluster. Tungsten mineralization exposed in this deposit can be divided into wolframite–quartz vein-type (63,000 t of WO₃) and greisen-type mineralization (40,000 t of WO₃) (Chen et al., 2018). The main sedimentary rocks exposed within the Maoping ore district are mainly Middle–Lower Cambrian low-grade metamorphosed sandstone and slate (Fig. 7c–d). The faults controlling the ore-bearing quartz veins are mainly divided into three groups: NE-, NW-, and EW-trending. A buried granitic intrusion was revealed at a depth of ~5 m in the mining area. The main intrusive phases are represented by a porphyritic biotite granite and a fine-grained muscovite granite (Chen et al., 2018). The LA-ICP-MS zircon U-Pb dating shows that the emplacement timing of the Maoping granitic intrusion was 159.0 ± 1.5 Ma (Chen et al., 2019a).

Wolframite–quartz veins at Maoping are mainly located in the contact zones between the monzogranites and sedimentary rocks (Fig. 7d). The ore and gangue minerals formed in these veins are dominated by abundant anhedral or subhedral quartz and wolframite, with various amounts of cassiterite, topaz, molybdenite, chalcopyrite, and sphalerite (Fig. 8c–d). Greisen-type W mineralization characterized by veinlets and dissemination are distributed in parts of the intensively altered granitic intrusion. Ore
minerals mainly comprise wolframite, cassiterite, and molybdenite. Based on in-situ U-Pb data from the cassiterite, Chen, et al. (2019a) proposed that the two types of mineralization formed from the same magmatic-hydrothermal event. The Maoping W deposit exhibits extensive hydrothermal alteration, involving greisenization, sericitization, silicification, and topazization. Sericitization, silicification, and topazization are mainly distributed along both sides of the ore-bearing quartz vein, while greisenization is mainly related to greisen-type mineralization, which is found on the cupola of the granite.

In South China, the Cretaceous W mineralization and related magmatism are weaker than those in the Jurassic. In the past few decades, only a small number of Cretaceous wolframite-quartz vein-type W deposits have been exposed, all with relatively small reserves, such as the Shanhu deposit in Guangxi and the Dajinshan deposit in Guangdong province (Fig. 1). The Shanhu W deposit is a typical wolframite-quartz vein-type hosted in Devonian elastic rocks (Fig. 9a, c-d). Mineralization at Shanhu mainly consists of wolframite and cassiterite in horizontal centimeter- to meter-scale quartz veins with lateral extents of hundreds of meters (Fig. 9b). A typical characteristic

Fig. 9. (a) Simplified geological map of the Shanhu tungsten deposit; (b) cross-sections along the main prospecting line in the Shanhu tungsten deposit; (c) wolframite-bearing quartz vein in the Shanhu W deposit; (d) sulfide distributed in the edge of the quartz vein.
feature of the Shanhui W deposit is the absence of granite within the depth exposed by the drill hole. However, the Yantianling granitic intrusion 3 km to the west shows highly consistent dates with the W mineralization in the Shanhui W deposit (Yu et al., 2014). The Re-Os date of molybdenite from the Dajishan W deposit is 84.93 Ma (Yu et al., 2012), indicating that metallogenesis is coeval with the Late Cretaceous igneous activity.

In recent years, a large-scale wolframite–quartz vein-type W deposit, named the Dongping, has been discovered in northern Jiangxi province, carrying 214,000 tons ofWO₃. In total, 162 typical wolframite-bearing quartz veins show typical vertical zonation characteristics and are mainly hosted in Neoproterozoic metamorphic rocks (Yang et al., 2018ab). The granite zircon U-Pb date shows that the associated granitic magma was emplaced at 133 Ma (Li et al., 2016), equivalent to Early Cretaceous. Different from the Late Cretaceous Shanhui and Dajishan W deposits located in the southwest of the Nanling region, the Dongping W deposit shares the same tectonic setting with the famous Dahutang W deposit in northern Jiangxi province.

3 Fluid Inclusion

Fluid inclusions in ore minerals reflect the physiochemical nature of the parental fluids present during the ore-forming process (Roedder, 1984; Wilkinson, 2001; Ni et al., 2015). In order to understand the properties, evolution and source of ore-forming fluids forming the wolframite–quartz veins in South China, we summarize here the published fluid-inclusion petrography and microthermometry data from several typical wolframite–quartz vein-type W deposits in South China and worldwide. Both wolframite- and quartz-hosted fluid inclusions were investigated with special attention given to the data from wolframite-hosted fluid inclusions available in a few particular deposits.

3.1 Fluid-inclusion petrography

According to the nature of the phase relationships at room temperature and the phase transitions during heating and cooling, three types of fluid inclusions are commonly recognized in wolframite and/or coexisting quartz samples, namely: two-phase aqueous inclusions (type L), two phase CO₂-bearing (type CB), and three-phase CO₂-rich inclusions (type C) (Figs. 10–12). All inclusion types were further subdivided by their host minerals into ‘Q’ for quartz, ‘W’ for wolframite and ‘F’ for fluorite.

3.1.1 Wolframite

Wolframite-hosted fluid inclusions from several deposits including Yaogangxian, Maoping, Piaotang, Dangping, Dajishan and Pangushan in the Nanling region all show two-phase liquid-rich features at room temperature. Primary-type L fluid inclusions from the Yaogangxian deposit exhibit circular, elongate, or negative-crystal shapes (plate-prismatic) (Fig. 10a–c). A few type CB inclusions were also identified in the Yaogangxian deposit, which consists of an aqueous phase and a dark vapor bubble at room temperature. Clathrates were detected during freezing runs and suggest CO₂-bearing fluid inclusions (Fig. 11). Wolframite samples from the Maoping deposit exhibit apparent crystal-growth zones and primary-type L fluid inclusions and are typically isolated within crystals or arranged along the growth zones (Fig. 10d–e). Type L inclusions are commonly tubular or sub-rounded in shape and from 8 to 30 μm in size, with liquid occupying 60–80% by volume. Similarly, type CB fluid inclusions can only be identified during cooling runs, when liquid CO₂ is condensed from the vapor phase.

Wolframite crystals from the Piaotang deposit only contain type L fluid inclusions, which are generally 20–60 μm in size. Primary inclusions mainly show tubular or needle-like shape, with a degree of filling for the liquid phase at 60–70% (Fig. 10f–g). Only primary-type L inclusions were identified in the wolframite from Dangping and these inclusions are generally 10–20 μm in size. They mainly show tubular shape, with a degree of filling at 70–80% (Fig. 10h–i).

Type L inclusions in wolframite from the Dajishan deposit are generally 10–30 μm in size and show tubular or elliptical shape (Fig. 10j–k). They are isolated or present along the growth zoning of a single wolframite grain, indicating a primary origin. Generally, bubbles occupying about 20% volume are observed in these inclusions. It is worth noting that no other type of inclusions has been observed in the Dajishan wolframite crystals, which is similar to the case in the Piaotang deposit. Only type L can be found in wolframites from the Pangushan deposit. These primary inclusions are generally 5–20 μm in size and show tubular or ellipse shape and appear to be filled to 70 to 90 volumetric percent with liquid phase (Fig. 10l).

3.1.2 Quartz

Two-phase liquid-rich inclusions and three-phase CO₂-rich inclusions are mostly commonly observed in quartz from wolframite-quartz veins. Type L fluid inclusions are prevalent in quartz associated with wolframite in the Yaogangxian deposit (Fig. 11a). They are variable in shape, including irregular, negative-crystal, and elongated, with typical size of 5 to 45 μm. Type C inclusions commonly have high CO₂-phase volumetric proportions (VCO₂ > 70%) and they usually occur in clusters with type L inclusions in quartz associated with wolframite (Fig. 11b). Type CB inclusions appear the same as the L type inclusion at room temperature, but are distinguished by the occurrence of liquid CO₂ phase during cooling runs. In the Maoping deposit, fluid inclusions in quartz can be divided into type L and type C (Fig. 11c–d), with estimated relative abundance of 85% and 15%, respectively. Type L inclusions are 6–40 μm in size and occur as both primary and secondary inclusions. They were observed as individual assemblages or coexisting with type C inclusions forming immiscible assemblages (Fig. 11d). In general, type C inclusions are characterized by CO₂ contents of 65%–85% by volume at room temperature.

Quartz coexisting with wolframite from the Piaotang deposit mainly contains type L inclusions that usually
have a degree of filling at 80–95% (Fig. 11e). The inclusions are 5 to 30 μm in size, and show irregular, negative-crystal and tabular shapes. Quartz from wolframite–quartz veins in the Dangping deposit also contains mainly type L inclusions, which usually consist of a large aqueous liquid, 85 to 95% volume fractions, and a small vapor phase (Fig. 11f). They are 5 to 35 μm in size, and commonly have negative-crystal and tabular shapes. In Dajishan, fluid inclusions in the quartz coexisting with wolframite are primarily of type L and type C, similar to those in Yaogangxian and Maoping. Fluid inclusions in the quartz from the Pangushan deposit contain predominantly type L inclusions.

3.2 Fluid-inclusion salinities and homogenization temperatures

3.2.1 Wolframite

Homogenization temperatures for type L\textsubscript{W} fluid
inclusions are in the range of 280°C to 360°C, peaking at around 300°C to 340°C in the Yaogangxian deposit (Fig. 13). Their final ice-melting temperatures range from −1.3°C to −4.8°C, corresponding to salinities from 2.2 wt% to 7.6 wt% NaCl equivalent (Fig. 13). In the Maoping deposit, homogenization temperatures for type Lw fluid inclusions are in the range 293°C to 360°C, peaking at around 300°C to 330°C (Fig. 13). Their salinities range from 2.2 wt% to 7.6 wt% NaCl equiv. (Fig. 13).

Type Lw inclusions in wolframite from the Piaotang deposit were measured and have ice melting temperatures from −5.8°C to −2.8°C, with salinities of 4.6 wt% to 8.9 wt% NaCl equiv. with vapor bubble disappearance at temperatures between 280°C and 390°C. Type Lw inclusions in wolframite from Dangping deposit showed that ice melting was measured at temperatures from −5.6°C to −4.2°C, with salinity values of 6.7 wt% to 8.7 wt% NaCl equiv. and vapor bubble disappearance at temperatures between 284°C and 324°C (Fig. 13).

Type Lw inclusions from wolframite in the Dajishan deposit have freezing points ranging from −5.8°C to −2.6°C, with salinities ranging from 4.3 wt% to 9.0 wt% NaCl equiv. (Fig. 13). They have homogenization temperatures between 240°C and 369°C (Fig. 13). Type Lw inclusions in wolframite from ores of the Pangushan deposit have final homogenization temperatures between 240°C and
366°C (Fig. 13). Their freezing points range from −5.1°C to −1.8°C and the salinities are between 3.1 wt% and 8.0 wt% NaCl equiv. (Fig. 13).
3.2.2 Quartz

During the main mineralization stage, primary-type L fluid inclusions in the quartz coexisting with wolframite from Yaogangxian yielded ice-melting temperatures from −2.5°C to −4.6°C, with salinities ranging from 4.2 wt% to 7.3 wt% NaCl equiv. (Fig. 13). They were homogenized to the liquid phase at temperatures of 244°C to 308°C (Fig. 13). In the Maoping deposit, homogenization temperatures for type L fluid inclusions in the quartz coexisting with wolframite range from 158°C to 318°C, peaking at around 200°C to 260°C (Fig. 13). Their salinities range from 0.7 wt% to 8 wt% NaCl equiv. (Fig. 13).

Type L inclusions in the quartz coexisting with wolframite from the Piaotang deposit have ice-melting temperatures from −4.2°C to −1.8°C, with salinities ranging from 3.1 wt% to 6.7 wt% NaCl equiv. (Fig. 13). Type L inclusions were homogenized to the liquid phase at temperatures of 171°C to 309°C. Type L inclusions in the quartz from ores of the Dangling W deposit have ice-melting temperature from −2.3°C to −0.7°C, with salinities ranging from 4.5 wt% to 8.5 wt% NaCl equiv. (Fig. 13). Their homogenization temperatures range from 180°C to 282°C.

Type L inclusions in quartz grains from the Dajishan deposit have ice melting temperatures from −5.7°C to −2.8°C, with salinities from 4.5 wt% to 8.8 wt% NaCl equiv. (Fig. 13). The homogenization temperatures of type I inclusions are between 170°C and 292°C. Ice melting in the ore stage type L inclusions in quartz from the Pangushan deposit occurred in the temperature ranging from −4.6°C to −1.8°C, corresponding to salinities from 3.1 wt% to 7.3 wt% NaCl equiv. (Fig. 13). These inclusions show homogenization to the liquid phase at temperatures between 150°C and 237°C.

4 Fluid Evolutionary Process and Metallogenic Mechanism

4.1 Fluid processes in quartz and coexisting wolframite

Much of the microthermometry data of fluid inclusions in wolframite and coexisting quartz from South China and abroad collectively show that the homogenization temperatures of wolframite-hosted fluid inclusions in most deposits are higher than those hosted in the coexisting quartz (Figs. 13, 14). Although few examples such as Xihuashan, St. Michael’s Mount and Cligga Head yield similar homogenization temperature ranges for fluid inclusions hosted in both minerals, wolframite-hosted fluid inclusions, except for the case of Cligga Head, consistently show a higher homogenization temperature in average. Based on detailed statistics on ore textures of wolframite–quartz vein-type W deposits in South China, we suggest that the wolframite crystals generally occur in the vein margin and were formed earlier than most intergrowth quartz (Ni et al., 2015; Li W X et al., 2018) (Figs. 6d, 8, 9c–d). This observation may well explain the differences in homogenization temperature between coexisting wolframite and quartz in the abovementioned cases.

However, the actual relationship between wolframite and coexisting quartz in wolframite–quartz veins can be more complex than previously recognized. In order to better determine the formation sequence of wolframite and coexisting quartz, scanning electron microscope–cathodoluminescence (SEM–CL) imaging was applied to distinguish different quartz generations and their paragenetic context (Pan et al., 2019). Based on detailed petrography and quartz CL imagining, at least four successive quartz generations, three independent wolframite mineralization events and five stages of muscovite precipitation are identified in a single sample from Yaogangxian deposit (Fig. 15). This result shows a paragenesis far more complex than that shown in previous comparable studies, and that wolframite-hosted inclusions do not necessarily exhibit higher homogenization temperatures than those from coexisting quartz, although some quartz-hosted fluid inclusions do have lower temperatures.

The combination of SEM–CL and single fluid-inclusion analysis in quartz and wolframite have yielded results permitting a greater understanding of the complex mineralization process of wolframite–quartz vein-type deposits (Pan et al., 2019). Test data on the Yaogangxian deposit demonstrate a clear relationship between quartz and wolframite deposition as the ore-forming fluid chemistry changed through time (Fig. 15). We suggest that the formation of hydrothermal wolframite-quartz veins might have experienced multi-stage fluid activities and so detailed petrography combined with SEM–CL imaging and fluid-inclusion microanalysis are critical for revealing the fluid evolution and metallogenic mechanism.

4.2 Sources of ore-forming fluids

Numerous studies over the last three decades have focused on the nature of the ore-forming fluid for wolframite–quartz vein-type W deposits (Campbell and Panter, 1990; Campbell and Robinson, 1990; Lueders, 1996; Bailly et al., 2002; Webster et al., 2004; Ni et al., 2006, 2015; Wei et al., 2012; Casanova et al., 2018; Li et al., 2018b; Chen et al., 2018; Yang et al., 2019a; Hulsbosch et al., 2016; Moura et al., 2014). An unresolved debate centers on whether mantle source material is added to ore-forming fluid. According to the traditional view, the granites related to W mineralization are typical continental re-melting or S-type (Chappell and White, 1974; Xu et al., 1982; Li et al., 2020). In addition, it is widely considered that large-scale metallogenic fluids closely related to W mineralization are derived mainly from the ancient crust. However, with the application of He–Ar and other rare gas isotopes in fluid-source tracing (Simmons et al., 1987; Matthews et al., 1987; Turner et al., 1990; Stuart et al., 1994), studies of some typical wolframite–quartz vein-type deposits show that mantle fluids clearly participate in the mineralization process (Stuart et al., 1995; Polya et al., 2000; Burnard and Polya, 2004). The He-Ar isotopic study of wolframite–quartz vein-type W deposits in South China also shows that mantle-derived fluids are involved in the mineralization process of some deposits and might be related to Sn, Cu and other associated mineralization, such as at Yaogangxian (Hu et al., 2012) and Meiziwo (Zhai et al., 2012), whereas some deposits such as Piaotang (Wang et al., 2009) and Tieshanlong (Li et al., 2012) show no
clear mantle source fluid involved.

The H and O isotopes of fluid inclusions are effective means to trace the contribution of ore-forming fluids from different sources (Ohmoto and Rye, 1970; Rye et al., 1974; Taylor, 1974). Previous studies, such as at Pato Buena in Peru (Landis and Rye, 1974), Panasqueira in Portugal (Kelly and Rye, 1979), Grey River in Canada (Higgins, 1985) and Chicote in Bolivia (Thorn, 1988), have shown that the main ore-forming fluids of wolframite–quartz vein-type deposits are magmatic in origin (Landis and Rye, 1974; Higgins, 1985; Thorn, 1988). In the late stage, such as at Jungbo, Suri and Deogma in South Korea (So and Yun, 1994), and Xihuashan, Dangping and Dajishan in Nanling (Zhang, 1987), different degrees of atmospheric water mixing are often recorded (Zhang, 1987; Shelton et al., 1987; So and Yun, 1994; Beuchat et al., 2004; Wei et al., 2012). In addition, some researchers have suggested that metamorphic fluids might have been involved in the mineralization of wolframate (Vallance et al., 2001; Rios et al., 2003).

Recently, studies of H–O isotopes in the main mineralization stage of the Yaoling, Meiziwo and Shirenzhang wolframite–quartz vein-type deposits suggested that both magmatic and meteoric fluids were the main source of ore-forming fluids (Jiang et al., 2019). This seems to be a common interpretation for many W deposits in adjoining southern Jiangxi. However, in the Yaogangxian deposit (Li et al., 2018b), reported that δD values of the extracted waters for wolframate and quartz samples in the ore-forming stage ranged from −45‰ to −67‰ and −56‰ to −64‰, respectively (Fig. 16). These values plot within the magmatic water region of the δD–δ18O diagram (Fig. 16), indicating a primary magmatic fluid for the mineralization process without any evident meteoric water involvement.

In conclusion, whether the formation of a wolframite–quartz vein-type deposit has significant mantle fluid contribution is still controversial. In addition, the H–O isotopic studies of fluid inclusions in previous studies were mainly focused on quartz, while direct constraints on wolframate, which can better represent the original ore-forming fluid, are relatively few. Recently, trace element ratios of a single fluid inclusion, such as Cs:Rb, combined with H–O isotopes have proved a powerful tool to constrain the source of ore-forming fluids (e.g., Korges et al., 2018; Pan et al., 2019), but so far only a few cases have been investigated.

4.3 The role of carbon dioxide for tungsten mineralization

The occurrence of CO2 in the formation of wolframite–quartz vein-type W deposits has been documented extensively in previous studies (Higgins, 1980; Higgins, 1985; Giuliani et al., 1988; So and Yun, 1994; Macey and Harris, 2006; Wang et al., 2010b; Wang et al., 2012b; Wei et al., 2012). However, most researches on the nature of ore-forming fluids was based on fluid inclusions entrapped in quartz (Giuliani et al., 1988; Wang et al., 2008; Jiang et al., 2019). In general, fluid inclusions hosted by ore minerals are better choices to investigate the P–T conditions of W precipitation, and gangue minerals may provide indirect information of the mineralization condition (Kouzmanov et al., 2010; Ni et al., 2015; Lüders 2017; Casanova et al., 2018; Korges et al., 2018; Ortelli et al., 2018; Li et al., 2018b; Chen et al., 2018; Pan et al., 2019). Summarized results show that the CO2 contents of fluid inclusions in wolframate and associated quartz from wolframate–quartz vein-type W deposits in South China

Fig. 15. Summarized petrographic relationship (a) and relative time sequence (b) between different mineral and fluid-inclusion generations in the studied sample; (c) summary plots showing average homogenization temperatures (T_h), salinities, and element concentration ratios X/(Na+K) of studied fluid-inclusion assemblages of Pw, Ps1–2, and Ps3 types. Abbreviations: wf = wolframate, qz = quartz, ms = muscovite, asp = arsenopyrite, chm = chamosite. (Color online)
show contrasting features. Fluid inclusions in quartz crystals from the Yaogangxian, Maoping, Dajishan, and Pangushan deposits contain abundant CO₂ whereas none was detected in fluid inclusions in quartz crystals from the Piaotang and Dangping deposits (Fig. 12). On the contrary, CO₂ was only recorded in wolframite from the Yaogangxian and Maoping deposits (Li et al., 2018b; Chen et al., 2018; Pan et al., 2019) (Fig. 11). According to these existing research results, we suggest that the CO₂ in ore-forming fluid is dispensable, which might depend mainly on the nature of the wall-rock. For example, CO₂-rich fluids occur in deposits with abundant carbonate in the host rock, such as at Yaogangxian, whereas there is no CO₂ in those deposits mainly composed of elastic rock, e.g., Piaotang and Dangping.

In the early literature, carbonate and bicarbonate complexes were suggested to have a contribution to W transport at very high fluid pressures (Higgins, 1980), and are conducive to W precipitation (Higgins, 1985; So and Yun, 1994). Based on a summary of previous work, Higgins (1980) considered that W in CO₂-rich fluid could migrate in the form of a carbonate–bicarbonate complex under conditions of high temperature and high pressure, which can easily explain the high concentration of CO₂ in fluid inclusions and the positive correlation between the concentration and grade of W mineralization. However, further studies argue that W exists in ore-forming fluids mainly as H₂WO₄, HWO₄⁻, and WO₄²⁻, which implies that carbonate complexes probably play a negligible role in hydrothermal tungsten transport (Wood and Samson, 2000). Nevertheless, the carbonate species might have indirect effects on W transportation and precipitation. For example, immiscibility may lead to the loss of CO₂ resulting in pH increase, which in turn reduces the stability of W in the hydrothermal fluid system (Wood and Samson, 2000), causing its precipitation (So and Yun, 1994; Wood and Samson, 2000). A similar process was also suggested to have contributed to gold precipitation in orogenic gold deposits (Phillips and Evans, 2004).

The detection of CO₂ in wolframite-hosted inclusions may indicate that wolframite was precipitated from a low-to-moderately-saline aqueous fluid containing minor amounts of CO₂. However, based on our results, the role of CO₂ in wolframite formation is still unclear. In general, type L_W inclusions are the dominant primary fluid inclusions in all the studied wolframite-quartz vein-type deposits. The microthermometric results for L_W-type inclusions indicate a decreasing trend in temperature (Fig. 14), suggesting that a simple cooling process could have caused the deposition of wolframite (Heinrich, 1990; Wood and Samson, 2000; Ni et al., 2015).

4.4 Ore precipitation mechanisms

Based on experimental studies, Wood and Samson (2000) emphasized the role of simple tungstate species (i.e. H₂WO₄, HWO₄⁻, WO₄²⁻) and alkali tungstate ion pairs in hydrothermal tungsten transport, because, in this case, the solubility of ferberite (FeWO₄) will reach a value as high as hundreds to thousands of parts per million. Clearly, the precipitation of the main tungstate ore minerals also requires a source supply of sufficient Fe, Mn, or Ca (e.g. Lecumberri-Sanchez et al., 2017). However, the precipitation process of W in hydrothermal fluid has been controversial for a long time. Various mechanisms have been invoked for W precipitation in wolframite-quartz vein deposits, including simple cooling of Fe–W-bearing fluids (Heinrich, 1990; O’Reilly et al., 1997; Ni et al., 2015), pressure decrease and boiling (Noronha et al., 1992; So and Yun, 1994), fluid mixing between magmatic fluids with cool and dilute meteoric water (Kelly and Rye, 1979; Samson, 1990; Yokart et al., 2003), and fluid-rock interaction (Lecumberri-Sanchez et al., 2017).

By reconstructing the P–V–T–X–O₂ evolution of H₂O-CO₂-CH₄ fluid in wolframite-quartz veins, Ramboz et al. (1985) suggested that cooling of ore-forming fluid leads to the formation of wolframite quartz vein. Ni et al. (2015) reported the infrared microthermometric data of fluid inclusions in coexisting quartz and wolframite in the Gannan metamorphic belt. An analogous simple cooling precipitation mechanism has been proposed based on the decreasing trend of homogenization temperatures with constant salinities (Fig. 14). Landis and Rye (1974) studied the fluid inclusions and stable isotopes of the Pasto Buena W polymetallic deposit, and revealed that the precipitation of W was caused by the mixing of meteoric water with magmatic water. Additionally, studies of fluid inclusion at Yaogangxian indicate that from the wolframite mineralization stage to late stage, the δD vs. salinity plots for type L fluid inclusions in quartz show a trend of dilution, which can be interpreted as mixing between a hot, saline fluid and a cooler diluted fluid (Chi and Savard, 1997; Li et al., 2018a). Fluid mixing is also indicated by the oxygen isotopic composition of fluids in the late stage, although δ¹⁸O values may be underestimated by using fluid-inclusion homogenization temperatures. During the sulfide-quartz vein stage, δD and δ¹⁸O values in quartz are relatively low (Fig. 16), and decreasing salinities are likely because of mixing. However, these processes all occurred in the post-mineralization stage, and consequently, only support that the fluid precipitated quartz had undergone immiscibility and mixing processes, whereas only simple fluid cooling was recorded in wolframite (Li et al., 2018a).

The experiments of Sondergeld and Turcotte (1979) revealed that fluid boiling is an important process of mineral precipitation in most hydrothermal deposits. Opening of faults results in pressure reduction and boiling fluid. The dispersion of some gases in the fluid can decrease the solubility of metal in the fluid, resulting in supersaturation and mineral precipitation. In addition, due to the escape of volatile components, such as CO₂, in the fluid system, the temperature of the ore-forming fluid decreases, and the pH value of the fluid rises significantly, resulting in instability in the complex and the precipitation of wolframite (Drummond and Ohmoto, 1985). Although boiling or unmixed fluid-inclusion assemblages are commonly observed in quartz but rarely reported in wolframite (Ni et al., 2015; Li et al., 2018b; Chen et al., 2018), a significant decrease in fluid trace-element concentrations of B, As and S in wolframite-hosted fluid inclusions strongly suggest that boiling fluid can be
concurrent with wolframite deposition (Fig. 16, Pan et al., 2019).

In conclusion, the study of fluid inclusions in wolframite–quartz vein-type W deposits reveals a variety of metallogenic mechanisms, and it is still an open question as to which mechanism plays a more important role in the ore precipitation process. CO₂ occurs in various amounts in most ore-forming fluids of W deposits. Further study is needed to clarify the roles of this component in the migration and precipitation of wolframite.

4.5 Fluid evolution and vertical zonation

The ‘five-floor vertical zonation’ prospecting model is characterized by the vertical zonation of vein–style ore bodies (Gu, 1984; Liu and Ma, 1993). This model has been used extensively in recent years by exploration geologists (Wang et al., 2010a; Xu et al., 2008). The model applies to orebodies made up of steeply dipping veins such as Meizhwo and Yaogangxian. Although of less abundance, ore veins with low dip angles also develop in some W deposits and can be of significant economic value, such as Maoping, Damingshan and Xushan (Wang et al., 2010a; Xu et al., 2008). To better understand the link between fluid evolution and vertical zonation, Chen et al. (2018) conducted fluid inclusion and H-O isotope study on the gently dipping veins of the Maoping W deposit. The results indicate that a slight spatial temperature gradient was recorded in the quartz. In contrast, fluid-inclusion data in wolframite are not spatially resolvable on the deposit scale. Similarly, H-O isotopes of fluid inclusion in wolframite from different zones are identical to magmatic water whereas meteoric water input was only recorded by quartz in the distal zone.

With increasing prospecting and exploration of wolframite–quartz vein-type W deposits, a new ‘five floors + basement’ model has been proposed (Xu et al., 2008; Wang et al., 2010a; Wang et al., 2019), which includes greisen-type mineralization at the bottom of vein systems. Both the ‘five-floor vertical zonation’ and the ‘five floors + basement’ models are prospecting rather than metallogenic models because they emphasize the spatial zoning of vein geometry and mineralization styles. Although geochronology data imply that the wolframite–quartz veins and the greisen-type mineralization at Maoping are the products of the same metallogenic hydrothermal event (Chen et al., 2019a), further study in terms of fluid chemistry are necessary to better understand the genesis.

4.6 Fluid inclusion LA-ICP-MS analysis

Advances in individual fluid-inclusion laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) enable analysis of elemental compositions of ore-forming fluids and have greatly improved our understanding of fluid properties and ore genesis (e.g., Heinrich, 1990, 2003; Ulrich et al., 1999; Audétat et al., 2000; Rauchenstein-Martinek et al., 2016; Wagner et al., 2016; Korges et al., 2018; Pan et al., 2019; Fiedrich et al., 2020). Several recent studies on wolframite–quartz vein-type deposits using fluid inclusion LA-ICP-MS analysis have greatly improved the understanding of the fluid properties and ore genesis (Lecumberri-Sanchez et al., 2017; Korges et al., 2018; Pan et al., 2019; Legros et al., 2019). By obtaining elemental composition of fluid inclusions associated with the main mineralization veins at the Panasqueira W deposit, Lecumberri-Sanchez et al. (2017) found that the Fe concentrations in the ore-forming fluid was inadequate to form large-scale wolframite, and further speculated that the Fe indispensable for wolframite precipitation was delivered by the wall rock during fluid–rock interaction.

Single fluid-inclusion LA-ICP-MS analysis also provides new insight for tracing fluid source and distinguishing genetic connection between different ore-mineralization styles (Samson et al., 2008; Korges et al., 2018). For example, the Zinnwald Sn–W deposit in Erzgebirge hosts both cassiterite in greisen bodies and subhorizontal cassiterite-wolframite quartz veins. To reveal whether the two diverse Sn–W mineralizations share an identical fluid source, Korges et al. (2018) carried out LA-ICP-MS analyses on fluid-inclusion assemblages in wolframite, cassiterite, and quartz samples from greisen and quartz veins. The similarity in fluid chemical compositions proved that ore-forming fluids containing elements required for diverse mineralization were generated from a single parental magmatic source and that the two mineralization styles are genetically linked. Moreover, Pan et al. (2019) used fluid composition to trace the fluid source of the Yaogangxian W deposit. The resulting Rb/Na vs. K/Na diagram exhibits a clear magmatic source for most fluid inclusions in both wolframite and quartz and the consistent fluid Rb/Cs ratios favor the dominance of a single sourced magmatic-hydrothermal fluid in the formation of the studied coexisting wolframite and quartz.

In summary, single fluid-inclusion LA-ICP-MS analysis and its combination with infrared microscopy allows composition determination of fluid inclusions hosted in both gangue and ore minerals, which offers great advantages in revealing fluid evolution, tracing fluid source and dissecting the ore precipitation process. However, only a few works have been done so far on wolframite–quartz vein-type deposits, which hampers further understanding on their ore-forming fluids and metallogenic mechanism.

5 Conclusions

(1) Fluid-inclusion microthermometry data statistics suggest that most wolframite in quartz vein-type W deposits tends to precipitate earlier than coexisting quartz. Detailed petrographic observation and CL imaging on the coexisting wolframite and quartz of the Yaogangxian deposit show repeated precipitation of quartz, wolframite, and muscovite, suggesting more complex fluid processes forming wolframite and quartz.

(2) Most previous studies suggested that the main ore-forming fluids of wolframite–quartz vein-type deposits display magmatic sources. Wolframite–quartz vein-type deposits in South China commonly contain variable CO₂, implying that CO₂ may have a positive effect on the transportation and precipitation of W.
(3) Integrated microthermometric studies indicate that wolframite was most likely deposited during cooling from an initial H₂O + NaCl ± CO₂ magmatic fluid in wolframite–quartz veins in South China. Fluid phase separation and mixing may also play an optimistic role in shifting ore-forming fluid conditions that are concurrent with wolframite deposition. We speculate that these factors determine the precipitation of W to various ore grades while the leading mechanism remains an open question.

(4) Comprehensive studies on spatial variation of fluid inclusions show that both the steeply and gently dipping veins are consistent with the ‘five floors’ model, which may have broader applications to exploration of wolframite–quartz vein-type deposits.

(5) Advances in individual fluid-inclusion laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) enable analysis of elemental compositions of ore-forming fluids and has greatly improved our understanding of the fluid properties and ore genesis. Single-fluid-inclusion LA-ICP-MS analysis also provides new insight for tracing fluid sources. In addition, large-enough fluid inclusions are generally preserved in quartz vein-type W deposits, which is the best research object for single inclusion analysis. Further application of this method to the research of wolframite–quartz vein-type deposit is promising and strongly encouraged.

Acknowledgments

This work is financially supported by a Key Project of the National Nature Science Foundation of China (Grant No. 41830426), and a National Key R&D Program of China Grant (No. 2016YFC0600205). The authors thank Ding Junying, Wang Guoguang and Chen Lili from Nanjing University for providing some of the figures. Susan Turner (Brisbane) assisted with English language.

Manuscript received Dec. 21, 2019 accepted Sept. 15, 2020 associate EIC: ZHOU Taofa edited by FEI Hongcai

References


About the first and corresponding author
NI PEI, Professor, Nanjing University. Professor Ni focuses on the study of ore deposits and geological fluids.