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Progressively released gases from fluid inclusions reveal new insights on W-Sn mineralization of the Yaogangxian tungsten deposit, South China

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ABSTRACT

The gentle stepwise crushing technique permits progressive extraction of gases from large, irregular, secondary fluid inclusions (SFIs) along micro-cracks to small, regular, liquid-rich primary fluid inclusions (PFIs). Previous studies have verified this general gas release pattern in different hydrothermal minerals based on the agreements between ⁴⁰Ar/³⁹Ar ages of the released gases from different crushing stages and the most likely corresponding geological events dated with other methods; and based on the excellent agreements between gas chemistry measured by QMS (quadrupole mass spectrometer) during stepwise crushing and the expected characteristics of SFIs and PFIs in the same samples acquired using Raman spectroscopy. In this study, we applied this QMS-based gentle stepwise crushing technique on ore and gangue minerals from the world-class Yaogangxian tungsten deposit in South China. Gases released from PFIs in cassiterite, wolframite, and quartz from ore-bearing veins show high CH₄, N₂, C₃H₈, and low CO₂, C₄H₁₀ contents, low CO₂/CH₄ (≪1) and high N₂/Ar (327–861 for ore minerals and 60.7-943 for quartzs from ore veins) ratios, along with multiple organic gaseous species. Their compositions resemble those of gases released from PFIs in quartzs from the Yaogangxian granites which represent magmatic-hydrothermal fluids that exsolved from the granitic magma. However, compared with these exsolved magmatic-hydrothermal fluids, ore mineral PFIs have relatively high He contents which indicate contributions from non-magmatic crustal fluids. This is consistent with high Ca^{2+} , low F^- concentrations, and low K⁺/Na⁺ (0.21–0.32) ratios observed in fluids in the quartz samples, as well as their relatively low water hydrogen isotopes (δD -H₂O = -102 to -59‰). These chemical characteristics, coupled with their magmatic sulfur (δ^{34} S-molybdenite and arsenopyrite = -0.2-1.4‰), methane hydrogen (δ D-CH₄ = -58 to -42‰), and fluid oxygen (δ^{18} O-H₂O = 3.9–5.1‰) isotopic compositions, indicate both magmatic and non-magmatic crustal components in the mineralizing fluids. Based on these observations and the low methane carbon isotope values $(\delta^{13}$ C-CH₄) in the studied quartz samples, we propose that fluid-rock interactions between the exsolved magmatic-hydrothermal fluids and the metasedimentary wall rocks played an important role in promoting W-Sn precipitation in this ore deposit. This study demonstrates the power of combining QMS-based stepwise crushing technique with traditional geochemical techniques in investigating ore-forming processes.

1. Introduction

Paleofluids trapped in fluid inclusions bear crucial information regarding the sources of fluids, the processes of fluid-rock interactions,

the chemical and physical conditions during ore formation as well as the timing and mechanism of mineralization (Roedder and Bodnar, 1980; Shepherd and Darbyshire, 1981; Kelley et al., 1986; Norman and Sawkins, 1987; Shepherd and Miller, 1988; Brown and Lamb, 1989;

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Roedder, 1997; Audétat et al., 1998; Yardley and Bodnar, 2014).

China is the world's largest tungsten producer. A significant percentage of China's known tungsten resources is distributed in the Nanling area, a major tungsten polymetallic metallogenic belt located at the central-southern region of the South China Craton. The Yaogangxian tungsten deposit is one of the most important granite-related world-class tungsten deposits in the Nanling Range. Numerous geological, geochronological, chemical and isotopic studies have been carried out on tungsten mineralization in this deposit (e.g., Zhang, 1987; Chen, 1988; Peng et al., 2006; Cao et al., 2009; Wang et al., 2010; Hu et al., 2012; Zhu et al., 2014; Li et al., 2015, 2017a; Yu et al., 2015). Geochronological studies including molybdenite Re-Os dating (Peng et al., 2006; Wang et al., 2010), hydrothermal mica ⁴⁰Ar/³⁹Ar stepwise heating (Peng et al., 2006; Xiao et al., 2019), and fluid inclusion ⁴⁰Ar/³⁹Ar stepwise crushing of wolframite, cassiterite, and vein quartz (Xiao et al., 2019) have constrained the timing of mineralization to 163-153 Ma. Microthermometric studies on wolframite and quartz suggest that the mineralizing fluids had intermediate temperature, low salinity, and low density, which correspond to a shallow metallogenic depth of 2.3-3.2 km (Dong et al., 2011; Wang et al., 2014; Yu et al., 2015; Li et al., 2017a). However, recent studies revealed far more complicated fluid evolution than previously thought. The formation of clathrates during freezing wolframite fluid inclusions led Li et al. (2017a) to propose that CO_2 is important in tungsten transport in this deposit. This view is at odds with the recent findings of Xiao et al. (2019), where progressive gas release patterns of fluid inclusions in cassiterite and wolframite showed that the mineralizing fluid is CH₄-rich rather than CO₂-rich, which in turn suggest that CO₂ played a negligible role in W-Sn mineralization. Existing isotopic data also led to different views on the nature of the mineralizing fluids. S–Pb isotopes (δ^{34} S = -2.6-3.9%, 206 Pb/ 204 Pb = 18.548-18.701, 207 Pb/ 204 Pb 15.691–15.811, 208 Pb/ 204 Pb = 38.809–39.212) of molybdenite, pyrite, arsenopyrite, and galena together with H–O isotopes of quartz (δD-H₂O = -59.9% to -53.8% and δ^{18} O-H₂O = 5.8% to 7.5% assuming homogenization temperature of 280 °C) suggest predominantly magmatic fluids in the source (Zhu et al., 2014). In contrast, He-Ar isotopic compositions of fluid inclusions in chalcopyrite, wolframite, pyrite, and arsenopyrite $({}^{40}\text{Ar}/{}^{36}\text{Ar} = 325-1191, {}^{3}\text{He}/{}^{4}\text{He} = 0.05-3.03$ Ra, where Ra denotes air ${}^{3}\text{He}/{}^{4}\text{He}$ ratio of 1.39 \times 10⁻⁶) suggest both nonmagmatic crustal and mantle-derived components in the fluids, indicating mixing between meteoric waters and exsolved fluids from the granitic magma which could have formed by crustal melting accompanied by crust-mantle interaction (Chen et al., 2011; Hu et al., 2012). Disagreements also exist regarding fluid processes that control local mineralization. For example, Cao et al. (2009) proposed that simple cooling led to wolframite formation while fluid mixing led to quartz formation. Later on, Dong et al. (2011) argued that simple cooling plus fluid mixing processes caused tungsten precipitation. More recently, Yu et al. (2015) suggested that fluid immiscibility was responsible for local mineralization.

Given that the deposit experienced complex hydrothermal evolution, as evidenced by the occurrence of multiple generations of fluid inclusions (Xiao et al., 2019), vastly different conclusions could be drawn if post-mineralization fluids cannot be distinguished from the oreforming fluids. This might be the root cause of the contrasting explanations of the mineralization process in the Yaogangxian tungsten deposit as it is almost impossible to distinguish volatiles of the primary fluid inclusions from those of the secondary fluid inclusions when they are extracted using traditional one-step/minor-step fast crushing or decrepitation techniques (Norman and Sawkins, 1987; Blamey, 2012). This seemingly unavoidable problem critically hindered the study of ore-formation (e.g., Villa, 2001; Qiu et al., 2002). Therefore, systematic investigation of different generations of fluid inclusions is a key to deciphering the fluid evolution of this complex mineral deposit.

Stepwise *in vacuo* crushing technique has been successfully applied in fluid inclusion gas compositional analyses for decades (Sarda et al.,

1985; Staudacher et al., 1989; Hopp et al., 2004; Buikin et al., 2014). For most hydrothermal minerals, hydrothermal perturbations after crystallization usually result in rapid entrapment of hydrothermal fluids which form secondary fluid inclusions with much larger sizes and more irregular shapes than primary fluid inclusions that form during mineral growth in a relatively stable fluid environment. The presence of these large secondary fluid inclusions is the biggest obstacle for accurate analyses of primary geofluids (Villa, 2001; Oiu et al., 2002). Using our stepwise crushing technique, different generations of fluid inclusions can be studied for their chemical compositions and geochronology. Earlier studies have suggested that this technique can effectively extract volatiles from different inclusion populations (Qiu and Jiang, 2007; Jiang et al., 2012; Buikin et al., 2016; Bai et al., 2018). For example, many ⁴⁰Ar/³⁹Ar dating experiments have shown that this technique preferentially extracts the large secondary fluid inclusions along microcracks in the initial crushing stage while gases from the smaller primary ones are mainly extracted in the final crushing stage, formation ages of both secondary and primary fluid inclusions can be therefore obtained (Qiu and Jiang, 2007; Jiang et al., 2012; Buikin et al., 2016; Bai et al., 2018; Xiao et al., 2019).

In this study, we focus on volatile compositions of fluid inclusions in the Yaogangxian tungsten deposit. Detailed microscopic observations and microthermometry were first performed on ore minerals cassiterite and wolframite and gangue mineral quartz, aiming to constrain the characteristics of different generations of fluid inclusions. Raman spectroscopic analyses were also carried out on semi-transparent cassiterite and transparent quartz to reveal the compositions of different types of fluid inclusions. The gas compositions of each generation of fluid inclusions in these minerals were further constrained using a stepwise crushing apparatus coupled with a quadrupole mass spectrometer. S isotopes of sulfides, H-O isotopes of fluids and H isotopes of methane in quartz samples were also investigated to further constrain the fluid chemistry of the deposit. Using both traditional approaches and the novel technique of combined QMS measurement with stepwise crushing, we report new results that provide novel insights on the evolution of fluids and the metallogenic mechanism of the Yaogangxian tungsten deposit.

2. Geological setting, sample descriptions, and characteristics of fluid inclusions

2.1. Geological setting

The South China Craton comprises the Yangtze Block in the northwest and the Cathaysia Block in the southeast (Fig. 1a). The Yaogangxian tungsten deposit is situated in the northwestern part of the Cathaysia Block in the central Nanling polymetallic metallogenic belt, an important polymetallic metallogenic belt in South China. Substantial amounts of large-scale W-Sn polymetallic deposits are found in the Nanling polymetallic minerogenic belt, most of which developed during the Middle–Late Jurassic (*ca.* 160–150 Ma, Hua et al., 2003; Mao et al., 2013). The polymetallic mineralization in this belt is associated with the regional Late Mesozoic granitic magmatic activities that are thought to be associated with the intra-continental extensional tectonic setting caused by the subduction of the Paleo-Pacific oceanic plate (Shu, 2007).

In the mining district of the Yaogangxian tungsten deposit, the oldest exposed stratum is a thick Cambrian *meta*-sandstone and slate succession (Fig. 1b), which mainly includes quartzose sandstone (most of them contain sericite and/or biotite), quartzo-feldspathic siltstone, slate, phyllite, greywacke, micaceous sandstone, quartzite, and argillaceous limestone (Chen, 1992). This succession is unconformably overlain by Devono–Carboniferous sandstone and limestone (Fig. 1b,c), which mainly consist of fine-grained argillaceous sandstone and quartzose sandstone with some shale, marlstone, and argillaceous limestone (Chen, 1992). Most sandstones in the region had metamorphosed to grey sericite-bearing quartzite while the limestones and shales didn't show



Fig. 1. Simplified geological map showing the location (a), geological characteristics (b, modified after Peng et al. (2006) and Zhu et al. (2015)) and metallogenic model (c, modified after Chen (1988)).

significant metamorphism (Qiu, 1984; Zhou et al., 2002). A young Triassic-Jurassic sandstone-dominated sequence overlies the Devono-Carboniferous sandstone and limestone layer (Fig. 1c). Coal-bearing layers and carbonaceous shales are locally present in the young sequence (Chen, 1992; Zhu et al., 2015). The Yaogangxian granites mainly intruded the Devonian and Cambrian strata (Chen, 1988). Veintype W-Sn ore bodies commonly occur along the contact zone between the outer zone of the granitic pluton and the surrounding Cambrian and Devono-Carboniferous rocks (Fig. 1c) (Chen, 1981; Lin et al., 1986). Greisenization and sulfidation alteration are common in the mining district, which developed widely along the contact zone between the ore-bearing veins and the meta-sandstone (Fig. A1 in Appendix A). Skarnization mainly occurred in the contact zone between the Devonian sandstone and limestone with the development of skarn-type scheelite mineralization in the Heshangtan region (Fig. 1b,c). Minor veinletdisseminated scheelite mineralization also developed in the Devonian calcareous sandstone (Fig. 1c). Other types of wall-rock alteration mainly include fluoritization, sericitization, carbonatization and local biotitization (Qiu, 1984).

The Yaogangxian tungsten deposit is spatially and temporally associated with the highly differentiated, S-type Yaogangxian composite granites (Fig. 1b). Based on the contact relationship, three stages of granite formation were proposed: the early-stage coarse-grained twomica granite or biotite granite, the second-stage medium- to finegrained two-mica granite, and the latest-stage fine-grained granite porphyry or muscovite granite (Li et al., 2011; Dong et al., 2014). Crystallization ages of these granites broadly fall within a range of 161–155 Ma (zircon U–Pb, Li et al., 2011, 2020). Molybdenite Re–Os ages (163–153 Ma, Peng et al., 2006; Wang et al., 2010), phlogopite and muscovite 40 Ar/ 39 Ar ages (155–153 Ma, Peng et al., 2006; Xiao et al., 2019), cassiterite and wolframite U–Pb ages (159–154 Ma, Deng et al., 2019; Li et al., 2020), as well as fluid inclusion 40 Ar/ 39 Ar ages (159–154 Ma) of wolframite, cassiterite, and quartz (Xiao et al., 2019) are considered reasonable estimates for the timing of W-Sn mineralization. It is generally accepted that the mineralization is associated with granite emplacement given the overlap in the timing of these two events (e.g., Li et al., 2011, 2020).

Wolframite mineralization in this deposit consists of predominant quartz-vein-type, subordinate greisen-type, and minor granite-type ores. Paragenetic sequence in the greisen-type ores consists of quartz, wolframite, muscovite and minor sulfides. Paragenetic sequence in the quartz-vein-type ores varies from different evolution stages. It typically consists of quartz, micas, wolframite, sulfides such as arsenopyrite, pyrite, and molybdenite, with some cassiterite in the wolframitecassiterite-quartz mineralization stage (W-Sn-Qtz stage) and quartz, micas, abundant sulfides including arsenopyrite, pyrite, chalcopyrite, sphalerite, and galena, with minor cassiterite in the subsequent sulfidequartz mineralization stage (Sulfide-Qtz stage) (Fig. 2). Molybdenite is generally found in the earlier W-Sn-Qtz stage whereas chalcopyrite starts to appear in the later W-Sn-Qtz stage and becomes abundant in the subsequent Sulfide-Qtz stage. Fluorites occur in many ore-bearing quartz veins (Fig. A2 in Appendix A).

2.2. Sample descriptions

To better understand the origin of the mineralizing fluids, different types of ore-bearing samples were collected (see Fig. A3 in Appendix A). Sample 13YGX10 is a greisen with few wolframite crystals. Sample 13YGX07 is a wolframite-bearing greisen-bordered quartz vein. Samples 13YGX05 and 13YGX17 are cassiterite-bearing quartz veins. Sample 13YGX28 is a wolframite-bearing quartz vein. All these samples show closely intergrown quartz, muscovite, wolframite and/or cassiterite, with variable amounts of sulfides (Fig. 3a–d). In the samples, ore mineral wolframite is generally idiomorphic-hypidiomorphic (Fig. 3a,b). Gangue mineral quartz generally directly contacts ore minerals with straight boundaries or fills wolframite and cassiterite (Fig. 3a–c), which indicates simultaneous or later formation of quartz. Sulfides, specifically chalcopyrite, usually fill ore minerals (Fig. 3b) or occur as cross-cutting veins (Fig. 3d), which indicates later formation.

Samples from the associated Yaogangxian granites were also collected to establish potential genetic links between the mineralization and the granitic intrusion. Sample 13YGX43 is a grey coarse-grained two-mica granite and sample 13YGX12 is a grey-to-white medium-grained two-mica granite. They mainly consist of plagioclase, K-feld-spar, quartz, biotite, and muscovite (Fig. 3e–f). These samples are relatively fresh, although there are slight sericitization of plagioclase and argillization of K-feldspar due to later hydrothermal events. Based

on field observations and categorization of Li et al. (2011) and Dong et al. (2014) (see Subsection 2.1), samples 13YGX43 and 13YGX12 correspond to early or intermediate stage granites in the mining district.

2.3. Characteristics of fluid inclusions

Fluid inclusions with different origins, i.e., primary or secondary, were identified within cassiterite, wolframite, and quartz samples (Figs. 4 and 5) based on the criteria of Roedder (1984) and Goldstein and Reynolds (1994). Primary fluid inclusions (PFIs) captured during mineral growth generally occur as three-dimensional clusters or along mineral growth zones. Secondary fluid inclusions (SFIs) captured during late hydrothermal perturbations generally distribute linearly along micro-cracks or healed micro-fractures. Some SFIs may occur as dense clusters away from micro-cracks. If fracturing occurs during the growth of the crystal, pseudosecondary fluid inclusions (PSFIs) may be trapped during continued crystal growth and thus seal ore-forming fluids.

In the current study, fluid inclusions with regular shapes in threedimensional clusters or along different growth bands and isolated fluid inclusions randomly distributed between the growth zones with no relationships with other fluid inclusion types are defined as PFIs (Figs. 4 and 5). They have regular shapes, small sizes (usually <15 µm in diameter except for minor large PFIs can be up to 30 µm in cassiterite), and similar vapor-filling degrees (f < 20%, f denotes the volume percentage of the bubble in the fluid inclusion) in the same mineral. Some regular fluid inclusions found along discrete trails within mineral grains are generally characterized as PSFIs (Fig. 5i). As they trap similar primary ore-forming fluids as the PFIs, these PSFIs are not distinguishable from the typical PFIs in microthermometric results and stepwise crushing experiments.

The SFIs in these minerals either distribute along healed or unhealed



Fig. 2. Paragenetic sequence of minerals in quartz-vein-type ores in the Yaogangxian tungsten deposit. The blue dotted line represents the dividing line of the earlier and later wolframite-cassiterite-quartz (W-Sn-Qtz) mineralization stages. The disappearance of molybdenite and the appearance of spatial association of W/Sn minerals with chalcopyrite represent the start of the later period of the W-Sn-Qtz mineralization stage. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 3. Representative photomicrographs of the studied samples. (a–b) Photomicrographs showing intergrown wolframite, quartz, and muscovite. (c) Photomicrograph showing intergrown cassiterite and quartz. (d) Late chalcopyrite vein crosscuts cassiterite. (e–f) Photomicrographs of the Yaogangxian granites. Micrographs of a, c and e were taken using plane-polarized light. Micrographs of b and d were taken using reflected light. Micrograph of f was taken using cross-polarized light. Mineral abbreviations: Qtz-quartz, Ms-muscovite, Wlf-wolframite, Cst-cassiterite, Ccp-chalcopyrite, Bt-biotite, Kfs-K-feldspar, Pl-plagioclase, Ser-sericite.



Fig. 4. Representative photomicrographs showing different types of fluid inclusions in the cassiterite samples (a–c) and wolframite samples (d–f). Infrared photomicrographs of wolframite-hosted fluid inclusions were taken using a ROLERA-XR digital camera. Some micro-cracks of minerals are represented by the dotted lines. Vapor-filling degrees (*f*) of the two-phase fluid inclusions are presented. L-aqueous solution. V-vapor phase, PFI and SFI represent primary and secondary fluid inclusion, respectively.

micro-cracks or occur as bead-like clusters (Figs. 4 and 5). Most of them show larger sizes (usually >20 μ m), irregular shapes, and various vapor-filling degrees (f = 5-95%) compared to the PFIs and PSFIs (Figs. 4 and 5). Some isolated fluid inclusions are large with irregular shapes or small necks (e.g., Fig. 4d). They likely have been modified during necking-down or partial H₂O leakage processes (e.g., Goldstein and Reynolds, 1994; Audétat and Günther, 1999; Van Den Kerkhof and Hein, 2001) and thus will be referred to as modified PFIs. The volume proportions of PFIs (including PSFIs) and SFIs in the studied minerals are estimated and summarized in Table 1. The SFIs in these minerals usually occupy a large

proportion of the fluid inclusions in the studied minerals, e.g., >50% in quartzs from the granites and greisen, $\sim40\%$ in quartz from the greisenbordered quartz vein, and 30–70% in minerals from the quartz veins. These proportions vary from sample to sample (Table 1), which, by itself, indicates different extents of late hydrothermal disturbances.



Fig. 5. Representative photomicrographs showing different types of fluid inclusions in the quartz samples from the granites (a–b), the greisen (c), the greisenbordered quartz vein (d), and the quartz veins (e–i). Expressions of *f*, L, V, PFI, and SFI are the same as those in Fig. 4. PSFI–pseudosecondary fluid inclusion, L_{CO2} -liquid CO₂, V_{CO2} -gaseous CO₂. Microthermometric results of three adjacent fluid inclusion assemblages are presented in order of homogenization temperatures (°C)/salinity (wt.% NaCl_{equiv}).

Table 1

Major fluid inclusion types and their proportions in different minerals.

Samples	Generation	PFIs		SFIs		Fine SFIs
	Composition	(aquo) CH ₄ -rich	(aquo) CO ₂ -rich	(aquo) CH ₄ -rich	(aquo) CO ₂ -rich	Unknown
	Phase correlation	Two-phase	Single-, two- or tri-phases	Two-phase	Single-, two- or tri-phases	Single-, two- or tri-phases
		L-rich	L- to V-rich	L-rich	L- to V-rich	L- to V-rich
Quartz samples	selected from the Yaoga	ngxian granites				
13YGX43Qtz	Proportion	~35%	_	~40%	~20%	<5%
	Diameter	<10 µm	_	<15 µm	10–20 μm	<5 μm
13YGX12Qtz	Proportion	~35%	_	~50%	<5%	~10%
	Diameter	1–10 µm	-	5–15 µm	10–20 µm	$<5~\mu m$
Quartz sample f	rom a greisen with a mi	neral association of qu	artz, muscovite and wolframite			
13YGX10Qtz	Proportions	~20%	~15%	<7%	~55%	<3%
	Diameter	${<}10\ \mu m$	10–15 µm	${<}20~\mu m$	10–30 µm	$<5~\mu m$
Quartz from a g	reisen-bordered quartz v	vein with a mineral ass	ociation of quartz, muscovite and	1 wolframite		
13YGX07Qtz	Proportion	~30%	~30%	$\sim 12\%$	~25%	<3%
	Diameter	${<}10\ \mu m$	$<\!\!15~\mu m$	${<}15~\mu m$	10–30 µm	$<5~\mu m$
Samples from or	re-bearing quartz veins v	with a mineral associat	ion of quartz, muscovite, sulfides	, cassiterite and/or wo	lframite	
13YGX05Cst	Proportion	~30%	_	~50%	~12%	~8%
	Diameter	<15 µm	_	<50 μm	<50 μm	<5 µm
13YGX17Cst	Proportion	~20%	-	~55%	~17%	~8%
	Diameter	<30 µm	_	<50 µm	<50 μm	<5 µm
13YGX17Qtz	Proportion	~30%	_	~15%	~52%	~3%
	Diameter	$<\!\!10~\mu m$	_	$<\!\!20~\mu m$	10–40 µm	$<5 \ \mu m$
13YGX28Qtz	Proportion	~70%	-	~7%	~20%	<3%
	Diameter	$<\!10~\mu m$	_	$<\!\!15~\mu m$	10–30 µm	<5 µm

Note: Proportions of different types of fluid inclusions were visually estimated. Wolframite samples were not analyzed because Raman analysis hasn't yet been applied to the opaque minerals. The symbol "–" denotes insignificant amounts or absent. Abbreviations: PFI-primary fluid inclusion, SFI-secondary fluid inclusion, aquoaqueous, Qtz-quartz, Cst-cassiterite, L-liquid, and V-vapor.

3. Analytical methods

3.1. Compositional analyses of individual fluid inclusions by Raman spectroscopy

A series of $\sim 100 \ \mu m$ thick double-polished fluid inclusion wafers of transparent quartz and semi-transparent cassiterite minerals were prepared for laser Raman compositional analyses. A HORIBA XploRA Plus Raman spectrometer was used to identify the compositions of individual fluid inclusions, at Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIG-CAS). An Ar⁺ ion laser (laser wavelength of 514.5 nm) was operated at 20 mW. The resolution was $\pm 1 \text{ cm}^{-1}$. Several gas species were identified by their Raman peaks: $CO_2 = 1387 \text{ cm}^{-1}$, $CH_4 = 2913-2917$ cm^{-1} , N₂ = 2327–2329 cm^{-1} . The A(CO₂/CH₄) values were calculated as area ratios of the Raman peaks of CO₂ and CH₄ using the software PeakFit (version v.4.12, Singh et al., 2011). The molar ratio (X_a/X_b) of two gas species can be calculated from their Raman peak area ratio $(A_a/$ A_b) through the equation of $X_a/X_b = (A_a/F_a)^*(A_b/F_b) = (A_a/A_b)^*(F_b/F_a)$; and the quantification factor (F-factor) is controlled by the Raman scattering cross-section and the spectral efficiency of the microspectrometer (Seitz and Chou, 1996; Burke, 2001). As the studied samples were measured with similar experimental conditions using the same instrument, it is reasonable to assume that the measured fluid inclusions in the same kind of mineral have nearly identical F-factor ratios, e.g., F_{CO2}/F_{CH4} . Therefore, it is possible to use the $A(CO_2/CH_4)$ values to infer the relative molar ratios of CO2 and CH4 of different types of fluid inclusions in the same kind of mineral.

3.2. Fluid inclusion microthermometry

A set of 100 µm-thick doubly polished wafers of ore-bearing veins was prepared for microthermometric measurements at State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, CAS. Measurements for cassiterite and quartz samples were performed on a Linkam THMSG-600 heating-freezing stage and measurements for wolframite were conducted on a Linkam THMSG-600 heating-freezing stage coupled with an OLYMPUS BX51 infrared microscope with a ROLERA-XR digital camera. Thermocouples were calibrated in the temperature range of -196 °C to 600 °C using synthetic fluid inclusions at the triple-phase point of CO₂ (-56.6 °C), the ice melting point of pure water (0 °C), and the critical point of H₂O (374.1 °C) (Shepherd et al., 1985). The uncertainties for high-temperature heating measurements are about \pm 0.2 °C for 0–100 °C and \pm 1 °C for 100–600 °C and the uncertainties for low-temperature cooling measurements are typically \pm 0.1 °C.

Salinities were calculated from the final ice melting temperatures (T_{m-ice}) for aqueous two-phase fluid inclusions with low vapor-filling degrees, using the equation of Hall et al. (1988): $w(\text{NaCl}_{eq}) = 1.78T_m - 4.42 \times 10^{-2} T_m^2 + 5.57 \times 10^{-4} T_m^3$, and the melting temperatures of clathrate $(T_{m-\text{Clath}}, \text{ Collins}, 1979)$ for CO₂-rich, aqueous-carbonic, two-phase fluid inclusions with higher vapor-filling degrees. For the CO₂-bearing tri-phase (L + L_{CO2} + V_{CO2}) carbonic inclusions, the CO₂ melting temperatures (T_{m-CO2}), T_{m-ice} , the homogenization temperature of the carbonic phases (T_{h-CO2}), and the homogenization temperature (T_h) were measured. The results are presented in Table B1 in Appendix B. It is important to note that the salinities of the CO₂-rich and CH₄-bearing, aqueous-carbonic fluid inclusions with high *f* values, either two- or triphase, were calculated assuming only CO₂ in the vapor, which would lead to an overestimation of clathrate melting temperature as some CH₄ is also present. As such, the calculated salinities are minimum estimates (Collins, 1979; Nwe and Morteani, 1993).

3.3. S-H-O isotopic analyses

3.3.1. S isotopes

Sulfur isotopic analyses were conducted on seven sulfide minerals including five arsenopyrite and two molybdenite samples. Sulfur isotopes were analyzed using a Delta-S mass spectrometer installed at Laboratory for Stable Isotope Geochemistry, Institute of Geology and Geophysics, CAS. The δ^{34} S of sulfide was determined on SO₂ according to the conventional combustion method of Robinson and Kusakabe (1975). Prior to analysis, a sulfide-CuO composite was loaded into a vacuum system and heated to 980 °C to produce SO₂. The analytical results are reported in standard delta notation relative to the Canyon Diablo Troilite (CDT) standard for S. The standard error is $\pm 0.2\%$ (1 σ). The results are presented in Table B2 in Appendix B.

3.3.2. H-O isotopes

Hydrogen and oxygen isotopic analyses were performed on five quartz samples selected from tungsten-bearing quartz veins, at the Stable Isotope Laboratory of the Institute of Mineral Resources, Chinese Academy of Geological Sciences.

The samples were first heated under vacuum at 150 °C for 24 h to remove gas impurities from cracks and surfaces of the minerals and some of the SFIs. Hydrogen isotopic composition of water within the fluid inclusions in quartz (expressed as δD -H₂O, ‰ V-SMOW) was determined by decrepitation at 600 °C. This temperature ensures the decrepitation of micron-sized PFIs while minimizes the decrepitation of nanometersized fine fluid inclusions because higher temperatures are required for fluids in fine fluid inclusions to exceed the mechanical strength of the host minerals and cause rupture of the inclusion walls (Kelley et al., 1986). As fine fluid inclusions could have distinct sources from the PFIs (Bodnar and Samson, 2003), their significant release at higher temperatures could potentially interfere with the chemical results of the PFIs. Water released from the fluid inclusions was purified and then reduced using carbon to produce H₂, which was further analyzed with a Finningan MAT 253 mass spectrometer. Helium was used as carrier gas. Methane was separated from the remaining gas mixture using a GSQ PLOT column, and then purified and converted to H₂ at 1400 °C. The resultant H₂ was introduced into the Finningan MAT 253 mass spectrometer so that ²H/¹H ratios of CH₄ (expressed as δD-CH₄, ‰ V-SMOW) could be obtained.

Oxygen was produced by reacting the quartz samples (20–30 mg) with the reagent BrF₅ at 500–680 °C for about 14 h. After removing other gas impurities using a cold trap, the purified O₂ was converted to CO₂ by reacting with graphite at 700 °C with the presence of a platinum catalyst. The CO₂ was purified and then analyzed using a Finnigan MAT 253 mass spectrometer to measure O isotopic compositions. The δ^{18} O-H₂O values were further calculated using the formula $\Delta_{(quartz-fluid)} = \delta^{18}$ O-SiO₂ – δ^{18} O-fluid = 3.34 × 10⁶/(T_h + 273.15)² – 3.31 (Matsuhisa et al., 1979) and the average homogenization temperatures (T_h) of the measured aqueous, two-phase, low-*f* fluid inclusions in quartzs from orebearing quartz veins.

Detailed analytical procedures for H–O isotopic analyses are the same as those described in Liu et al. (2013). The analytical results are reported in standard delta notation relative to the Vienna Standard Mean Ocean Water (SMOW) standard. The standard errors (1 σ) are \pm 1‰ for H and \pm 0.2‰ for O. The results are presented in Table B3 in Appendix B.

3.4. QMS (quadrupole mass spectrometer)-stepwise crushing on gas compositional analyses

Ore minerals wolframite and cassiterite from quartz-vein-type ore veins and quartz from various types of rocks were selected for gas compositional analyses using an SRS© RGA200® quadrupole mass spectrometer (QMS) at the State Key Laboratory of Isotope Geochemistry, GIG-CAS. The measurement precision is between 0.3 and 0.5%

RSD. The QMS is equipped with a Faraday cup and an electron multiplier. It has a mass range of 1-200 amu (mass to charge ratio). An inhouse designed crushing system (Qiu and Wijbrans, 2006; Qiu and Jiang, 2007; Qiu et al., 2011) was connected to the QMS to progressively extract gases from the fluid inclusions. The crushing system consists of a crusher and a Pfeiffer HiCube80 Eco® turbo pumping station. The crusher comprises a type 316L stainless steel tube (length: 160 mm, inner diameter: 28 mm) with a spherical curvature on the internal base and a magnetic 3Cr13 type (or S42030) stainless steel pestle. The pestle (weight: 214 g) was controlled by an external electric magnet with a frequency of 2.5 Hz. An adjustable repeating-timer-relay was used to control the magnet for repeatedly lifting and dropping of the pestle from a height of 3–5 cm in order to crush the minerals with gentle crushing strength. The crushing strength is more than one-order-of-magnitude lower than those of traditional crushing devices of Matsumoto et al. (2001).

Mineral samples (250–840 μ m in size) were carefully hand-picked under a binocular microscope and rinsed several times with deionized water and dilute nitric acid in an ultrasonic bath to remove surface organics. Dried mineral grains (~150 mg for each sample) and the pestle were loaded at the bottom of the crushing tube in sequence. The crushing system was then baked at 150 °C using a furnace and the connecting tubes were baked at 200 °C using heat tapes for 20 h to remove gas impurities absorbed by the surface of the metal tubes. Prior to the experiments, a high vacuum condition (4.0 \times 10⁻⁸ mbar) was obtained using the turbo pump. The experiments were performed at room temperature. A blank measurement was carried out before each sample measurement in static mode without the movement of the pestle rather than dynamic mode where the pestle crushes an empty tube because crushing the empty tube could generate a significant amount of gases (Graney and Kesler, 1995). This effect is greatly reduced during sample measurement due to buffering by mineral grains (Blamey, 2012). Blanks measured in the static mode, therefore, should be more suitable than a dynamic blank. During the experiments, the extraction line was isolated from the vacuum pump and the analysis system. Gases released by crushing were introduced into the QMS immediately after crushing and then analyzed using the Faraday cup in static mode. A histogram scan mode was applied to rapidly scan the mass range of 1 to 65 amu. The electron energy and ion energy used for electron impact ionization were set at 70 eV and 12 eV, respectively.

Gas species were identified based on their standard fragmentation patterns from the RGA (Residual Gas Analyzer) software library. When several gas species show overlapping peak patterns, their strongest peaks with the least interferences from other gas fragments were chosen for quantification. The fragmentation patterns stored in the RGA software library were used for conversion. Based on standard fragmentation patterns, the current QMS allows a qualitative and semi-quantitative determination of the concentrations of major gaseous species through fast and continuous data acquisition. After each measurement, the entire system was opened to the turbo pump for cleanup. The analytical procedures are similar to those described in Xiao et al. (2019). The results are presented as relative contents in Table B4 in Appendix B.

4. Results

4.1. Fluid inclusion petrography and Raman analyses

Raman analyses were only applied to semi-transparent cassiterite and transparent quartz. Gas compositions of different types of PFIs and SFIs are summarized and presented in Table 1. Representative fluid



Fig. 6. Representative Raman compositions of vapor phases of primary and secondary fluid inclusions within different minerals. The $A(CO_2/CH_4)$ ratio represents area ratios of the Raman peaks of CO_2 and CH_4 calculated using the software PeakFit (version v.4.12, Singh et al., 2011).

inclusion types with their Raman spectra are presented in Fig. 6 and Fig. A4 in Appendix A.

4.1.1. Fluid inclusions within cassiterite and wolframite

Fluid inclusions within cassiterite and wolframite exhibit similar features and are predominantly aqueous two-phase (Fig. 4). PFIs are relatively small (generally <15 µm but some PFIs in cassiterite can be up to 30 µm). They usually display relatively regular shapes (Fig. 4a, d&e). For example, PFIs in the cassiterite are elongated and tubular with low vapor-filling degrees (f = 6-10%, Fig. 4a), whereas those in the wolframite are elongated or near-circular with similarly elevated vaporfilling degrees (f = 16-20%, Fig. 4d,e). Modified PFIs with large sizes and irregular shapes (e.g., Fig. 4d) are sporadically distributed in the minerals. SFIs distribute linearly and generally have larger sizes (mostly >20 µm) as well as more irregular shapes relative to PFIs (Fig. 4b,f). Gasrich SFIs and secondary gas inclusions are limited (Fig. 4). In addition to the large SFIs, abundant fine SFIs with sizes varying from several micrometers to nano-scale occurring as clusters or trails also developed, in particular, in the cassiterite samples (Fig. 4c). These trails of SFIs probably resulted from post-entrapment changes of big fluid inclusions such as necking-down or stretching (e.g., Goldstein and Reynolds, 1994), or they could have formed during post-mineralization hydrothermal perturbations (Lu et al., 2004). No CO₂-bearing tri-phase fluid inclusions were observed in the cassiterite and wolframite samples.

The PFIs and most SFIs within the cassiterites are typically aqueousmethanoic or methanoic (expressed as (aquo) methanoic) with high CH_4 and low to negligible CO_2 contents (Fig. 6a,b). Minor (aquo) CO_2 -rich SFIs or modified fluid inclusions with higher vapor-filling degrees and *A* (CO_2 / CH_4) ratios (>1) are also present (Fig. 6c).

4.1.2. Fluid inclusions within quartzs from the Yaogangxian granite

Two groups of two-phase fluid inclusions are identified in quartzs from the Yaogangxian granites (Fig. 5a,b). The first group, which we infer as PFIs, predominately consists of fluid inclusions with isolated distributions. These PFIs have regular shapes but are very small (only several micrometers in size, Fig. 5a). They are typically (aquo) methanoic (Fig. 6d). The second group, which we infer as SFIs, can occupy 60% of the fluid inclusions in the quartzs. They mainly distribute along trails or micro-cracks that crosscut the grain boundaries of the host quartz grains, indicating secondary origin. These SFIs are relatively large (around 10–20 μ m in size) with irregular shapes (Fig. 5a,b). They are mainly (aquo) methanoic (Fig. 6e). In addition, abundant fine SFIs developed along mineral micro-cracks, which are best exemplified by sample 13YGX12Qtz (Fig. 5b). These fine SFIs are too small to be analyzed by Raman spectroscopy.

Fluid saturation during magma evolution is an essential step for the redistribution of volatiles and the formation of economic enrichments of W, Sn, and many other metals (Cline and Bodnar, 1991; Lowenstern, 1994; Audétat et al., 2000a; Thomas et al., 2005). From the initial fluid saturation in a crystallizing melt to the final solidification of the residual melts, the magmatic-hydrothermal system transforms entirely from a high-temperature magmatic stage to a hydrothermal stage. This process (termed magmatic-to-hydrothermal transition) is characterized by the transition of melt + crystal \rightarrow melt + crystal + volatile \rightarrow fluid. The resulting melts and fluids could potentially be trapped by the diagenetic minerals such as quartz and feldspar during crystallization, as melt inclusions, melt-fluid inclusions, or fluid inclusions (Audétat et al., 2000a; Lowenstern, 2003; Roedder, 2003; Rickers et al., 2006). Among these, PFIs are the most direct representation of the exsolved magmatic fluids (Fulignati et al., 2011; Liu et al., 2021). The host granite rocks could also have been affected by a series of fluid influxes during later alteration and hydrothermal disturbances, which would form a large number of SFIs along planes or micro-cracks (Dobeš, 2005; Conliffe and Feely, 2010). Therefore, the fluids trapped in the observed isolated PFIs and SFIs represent magmatic-hydrothermal fluids exsolving from the Yaogangxain granitic magma and later-stage hydrothermal fluids,

respectively.

4.1.3. Fluid inclusions within quartz from ore-bearing veins

Fluid inclusions within quartz samples show variable features (Table 1). For vein quartzs that are closely associated with ore minerals (e.g., 13YGX17Qtz and 13YGX28Qtz), the PFIs are aqueous two-phase with low vapor-filling degrees (Fig. 5e-i), and compositionally (aquo) methanoic (Fig. 6f). In contrast, for quartzs from the greisen and greisenbordered quartz vein with minor to negligible ore minerals (e.g., 13YGX10Qtz and 13YGX07Qtz), their PFIs have distinct vapor-filling degrees (Fig. 5c,d) and include aqueous and gas-rich two-phase as well as CO2-bearing tri-phase inclusions, which imply fluid immiscibility, also known as multiphase multicomponent equilibrium (e.g., Ramboz et al., 1982). The Raman results of PFIs in quartz samples with signs of fluid immiscibility show higher A(CO₂/CH₄) ratios with increasing vapor-filling degrees (Fig. A4). Broadly speaking, the smaller PFIs in these quartz samples are (aquo) methanoic with low vapor-filling degrees whereas the larger ones with higher vapor-filling degrees are (aquo) CO₂-rich (e.g., Fig. 6g).

The SFIs in these quartzs widely developed along mineral microcracks. They generally have larger sizes and irregular shapes (Fig. 5c, e&f). They also include aqueous and gas-rich two-phase, CO₂-bearing tri-phase, and pure gas inclusions that contain mostly CO₂ with minor CH₄. These SFIs are mainly (aquo) CO₂-rich with $A(CO_2/CH_4)$ ratios > 1 (Fig. 6h,i).

4.2. Microthermometry of fluid inclusions in cassiterite, wolframite, and quartz

Both primary and secondary fluid inclusions in spatially coexisted cassiterite, wolframite, and/or quartz from ore-bearing veins were selected for microthermometric measurements to characterize the temperature and salinity of the fluids during different evolution stages of the deposit. The granite samples were not measured because of the small volumes of their PFIs (mostly <4 mm), which limit the accuracy of microthermometric measurements.

Measurements of fluid inclusions with primary origin were performed on fluid inclusion assemblages (FIAs, Goldstein and Reynolds, 1994) which include PFIs along growing zones and PSFIs along discrete inner-crystal fractures. PFIs in three-dimensional clusters with similar shapes and visually approximate phase ratios, as well as isolated PFIs were also measured. Data on single FIAs with homogenization temperatures within 15 °C and single PFI clusters with similar homogenization temperatures were considered valid based on the criteria of Goldstein and Reynolds (1994) and Chi and Lu (2008). The scopes and average values of the microthermometric data of each FIA and the distribution characteristics of all the measured fluid inclusions are presented in Table B1. Modified PFIs, especially those with small necks, and FIAs with various shapes and f values resulted from heterogeneous trapping are avoided in the compilation and the model calculation.

4.2.1. Microthermometry of ore minerals cassiterite and wolframite

Two-phase PFIs in cassiterites from the earlier W-Sn-Qtz mineralization stage characterized by the occurrence of molybdenite and the absence of chalcopyrite in the ore veins (Fig. 2) have T_h (homogenized to the liquid phase, expressed as LV–L in the following texts) values varying from 304 to 333 °C (peaking at 304–310 °C and 320–330 °C, Fig. 7a) and T_{m-ice} values ranging from –2.0 to –5.1 °C, which correspond to salinities of 3.4–8.0 wt% NaCl_{equiv}. (Fig. 7b). Those from the later W-Sn-Qtz mineralization stage characterized by the disappearance of molybdenite and the occurrence of chalcopyrite in the ore veins (Fig. 2) have T_h (LV–L) values of 256–316 °C (peaking at 280 to 290 °C, Fig. 7a) and T_{m-ice} values ranging from –1.9 to –2.5 °C, which correspond to salinities of 3.2–4.2 wt% NaCl_{equiv}. (Fig. 7b). Two-phase SFIs have T_h (LV–L) values varying from 209 to 240 °C and T_{m-ice} values ranging from –1.1 to –2.2 °C with salinities of 1.9–3.7 wt% NaCl_{equiv} (Fig. 7a,b).



Fig. 7. Microthermometric results. Histograms of homogenization temperatures (T_h) and plots of T_h vs. salinity of aqueous two-phase fluid inclusions in cassiterite (a–b), spatially coexisting minerals (c–d), and different types of fluid inclusions in quartz from ore-bearing quartz veins (e–f).

Two-phase PFIs in wolframite have $T_{\rm h}$ (LV–L) values of 249–315 °C, peaking at 250 to 270 and 280 to 290 °C (Fig. 7c). Their $T_{m\text{-ice}}$ values range from -1.5 to -4.2 °C, which correspond to salinities of 2.6–6.7 wt % NaCl_{equiv}. (Fig. 7d). Minor CO₂-rich two-phase PFIs with larger sizes and higher vapor-filling degrees were also observed in the wolframite based on the occurrence of clathrates during freezing. They are homogenized to the liquid phase at 271–313 °C. Their $T_{m\text{-Clath}}$ values are 5.9–6.3 °C, which correspond to salinities of 6.9–7.5 wt% NaCl_{equiv}. (Table B1).

4.2.2. Microthermometry of gangue mineral quartz

Different types of PFIs in quartz samples from ore-bearing quartz veins are measured (Fig. 7e,f). Low-*f* (<10%, Table B1) two-phase PFIs, which are mainly (aquo) CH₄-rich, are homogenized to the liquid phase at 230–294 °C, clustering around 230–280 °C (Figs. 5i and 7e). Their $T_{m.ice}$ values range from -1.1 to -3.7 °C, corresponding to salinities of 1.9–6.1 wt% NaCl_{equiv}. (Fig. 7f).

Two-phase PFIs in the quartz samples with higher *f* values (10–20%), which are mainly (aquo) CO₂-rich, were also measured. They are homogenized to the liquid phase at 264–333 °C (Fig. 7e). Their $T_{\text{m-Clath}}$ values are 6.0–9.3 °C, corresponding to salinities of 1.4–7.4 wt%

NaCl_{equiv.} (Fig. 7e). Some high $T_{\text{m-Clath}}$ values >10 °C were also observed among these CO₂-rich two-phase PFIs. This was likely caused by the presence of some other dissolved gas species, e.g., CH₄, in the fluid inclusions, which hinders salinity determinations. CO₂-rich tri-phase PFIs in these quartzs are homogenized to liquid or gas phases at 323–395 °C with $T_{\text{h-CO2}}$ of 25.1–30.1 °C. The melting temperatures of the solid CO₂ ($T_{\text{m-CO2}}$) range from -57.6 to -57.4 °C, which are slightly lower than the triple point of pure CO₂ at -56.6 °C, indicating the presence of other dissolved gases in addition to CO₂ in these fluid inclusions. Clathrate melting occurs at 9.3–10.7 °C. Some high $T_{\text{m-Clath}}$ values (>10 °C) agree with the presence of other dissolved gas species in fluid inclusions.

A group of relatively large, liquid-rich, two-phase CO₂-rich SFIs is also measured. They are homogenized to the liquid phase at 195.6–228.8 °C (Fig. 7e). Their T_{m-ice} values range from -0.8 to -3.2 °C, corresponding to salinities of 1.4–5.3 wt% NaCl_{equiv}. (Fig. 7f).

4.2.3. Validity assessment of the microthermometric data

The measured homogenization temperatures and salinities of isolated PFIs approximate those of PFI clusters and FIAs (Table B1), which supports the validity of the data based on the criteria of Chi and Lu (2008) and Chi et al. (2021).

The major $T_{\rm h}$ peaks of aqueous CH₄-rich PFIs in cassiterite, wolframite, and quartz migrated towards lower values with relatively wide ranges of 77 °C, 66 °C, and 64 °C, respectively (Fig. 7c). The similar shapes and the similarly low f values (6-10% for cassiterite, 10-20% for wolframite, and 3-10% for quartz) of these measured fluid inclusions rule out the scenario of heterogeneous-trapping. Instead, continuous mineral growth during the protracted cooling process of the ore-forming fluids as a result of multiple episodes of magma intrusion into the composite plutons is more likely the cause for the wide range of observed Th values. For example, cassiterites in granite-related W-Sn deposits generally have multiple generations of growth as suggested by distinct regions with different brightness in their CL images (Zhang et al., 2011, 2017). W-Sn minerals can crystallize across a wide range of fluid temperatures (e.g., >100 °C), as reported in many case studies (e. g., T_h -Wlf = 256–380 °C and T_h -Cst = 292–398 °C, Campbell and Panter 1990; $T_{\rm h}$ -Sch = 151–337 °C, Zhu and Peng 2015). PFIs in wolframite in Jurassic granite-related W-Sn deposits in South China are cases in point (e.g., T_h -Wlf = 280–390 °C in Piaotang W deposit; T_h -Wlf = 240–369 °C in Dajishan W deposit; $T_{\rm h}$ -Wlf = 240–366 °C in Pangushan W deposit; $T_{\rm b}$ -Wlf = 239–380 °C in Xihuashan W deposit; Wei et al., 2012; Ni et al., 2015).

In contrast, the much larger ranges of $T_{\rm h}$ values and salinities of the aqueous, CO₂-rich, two- and tri-phase PFIs in the quartz samples likely resulted from heterogeneous trapping and variable contents of CH₄ in the fluid inclusions. These values, therefore, cannot be used to estimate the physical conditions of the quartz growth.

4.3. S-H-O isotopic compositions

Sulfur isotope values (δ^{34} S) of five arsenopyrite and two molybdenite samples selected from W-Sn bearing quartz veins span from -0.2% to

1.4‰ (Table B2). Five quartz samples selected from similar quartz veins were analyzed for hydrogen and oxygen stable isotopes. These samples yielded a wide range of fluid δ D-H₂O values from -102% to -59% and relatively uniform methane δ D-CH₄ values from -58% to -42% (Table B3). Their δ^{18} O-SiO₂ values fall within a limited range of 12.5–13.7‰. The calculated δ^{18} O-H₂O values of the fluids range from 3.9‰ to 5.1‰ using the equation of Matsuhisa et al. (1979) when an average homogenization temperature of 256 °C of the quartz samples was used.

4.4. QMS gas compositional analyses

We analyzed the following samples with QMS for their fluid inclusion gas compositions: two quartz samples (13YGX43Qtz and 13YGX12Qtz) from the Yaogangxian granites; a quartz sample (13YGX10Qtz) from a greisen; a set of intergrown quartz (13YGX07Qtz) and wolframite (13YGX07Wlf) from a greisen-bordered quartz vein; a cassiterite sample (13YGX05Cst), a quartz sample (13YGX28Qtz), together with a set of intergrown quartz (13YGX17Qtz) and cassiterite (13YGX17Cst) from ore-bearing quartz veins. The results are presented in Table B4, Figs. 8–12, and Fig. A5 and A6 in Appendix A. In general, fluid inclusions in the studied minerals mainly contain CO_2 , CH_4 , H_2O , N_2 , some other light hydrocarbons such as ethane, propane, and butane, plus minor He, Ar, and O_2 .

Even though the investigated minerals come from different rock types, they exhibited comparable compositional features as revealed by the crushing experiments. Overall, gases released in the initial crushing stages have systematically different compositions compared to those from the final crushing stages for almost all studied samples (Figs. 8–11). In general, gases extracted from the initial crushing stage are characterized by high CO_2 contents with CO_2/CH_4 ratios > 1 (Figs. 8 and 9). In



Fig. 8. Plots showing the variations of gaseous CO_2/CH_4 ratios during stepwise crushing. The shadows with different filling colors represent the different crushing stages. The orange shadow in Fig. 8b represents a crushing stage with volatile compositions that are distinct from any other crushing stages. "Drops" represents the pestle drop numbers during crushing, which are presented in Table B4. The pestle drop numbers and potential gas sources of each crushing stage are also shown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 9. Plots showing the variations of CO₂, CH₄, N₂, and water contents during stepwise crushing. The expressions of drops and crushing stages are the same as those in Fig. 8.



Fig. 10. N₂–CO₂–CH₄ ternary diagrams showing different compositions of gases from each crushing stage. The crushing steps included in different crushing stages of each sample are the same as those in Fig. 8.

contrast, gases extracted from the final crushing stage are marked by high CH₄ and minor to negligible CO₂ contents with CO₂/CH₄ ratios < 1 (Figs. 8 and 9) as well as higher contents of C₃H₈ (with the exceptions of the cassiterite samples) and lower contents of C₄H₁₀ (Fig. A5). Additionally, an intermediate stage with high H₂O contents and gradually decreasing CO₂/CH₄ ratios can also be identified for each sample (Figs. 8 and 9). The release patterns of H_2O generally start with very low contents in the initial crushing stage, which progressively increase during the course of crushing and reach peak values in the intermediate or final crushing stage (Fig. 9).

Compositional variations of gases extracted from quartzs from the Yaogangxian granites are quite different. For example, quartz sample



Fig. 11. Plots of N_2/Ar versus CO_2/CH_4 ratios. This discrimination diagram is developed by Norman and Moore (1999) and improved by Blamey (2012) to distinguish the origins of volatiles captured by fluid inclusions. Meteoric fluids typically have low N_2/Ar ratios that are similar to air-saturated water (ASW, $N_2/Ar \sim 38$; Norman and Musgrave, 1994) and high CO_2/CH_4 ratios (>1, due to their low CH_4 concentrations). Magmatic fluids generally have N_2/Ar ratios 100 to 1000 times higher than ASW (Giggenbach, 1996; Norman and Moore, 1999). Crustal fluids represent meteoric fluids approximatively in equilibrium with crustal rocks, they may acquire crustal methane, which would lower their CO_2/CH_4 ratios (Blamey, 2012). Organic crustal fluids represent meteoric fluids approaching equilibration with crustal rocks that were contaminated by organic species derived from wall rocks. Evolved magmatic fluids represent composite fluids that consist of various proportions of volatiles from magmatic, crustal, and/or meteoric sources.



Fig. 12. N_2 -Ar-He ternary diagrams for ore mineral wolframite. The N_2 -Ar-He diagram was first developed by Giggenbach (1986) and Norman and Musgrave (1994). N_2 /Ar ratios of "Air" and "ASW" (Air Saturated Water, *ca.* 38) are indicated. The field of "magmatic water" is from Giggenbach (1986). Data of wolframite sample 13YGX06Wlf are from Xiao et al., (2019).

13YGX12Qtz is characterized by high contents of CH₄ and constantly low CO_2/CH_4 ratios (<1) throughout the whole experiment (Fig. 8b). More interestingly, its CO_2/CH_4 ratios gradually declined for the first 15 crushing steps, remained stable at extremely low levels (with an average ratio of 0.09) for the middle crushing steps (Steps 16–28) and then increased slightly (up to 0.56) for the last several crushing steps (Steps 29–36). A significant rebound of the tail of the CO_2/CH_4 ratios is also observed in the cassiterite samples 13YGX05Cst and 13YGX17Cst (Fig. 8h,i).

5. Discussion

5.1. Gas compositions of different fluid inclusion groups

Using a similar crushing technique, previous studies (Qiu and Jiang, 2007; Jiang et al., 2012; Bai et al., 2013) have established that most large SFIs distributed along mineral micro-cracks can be easily extracted in the initial crushing stage while the gases released in the final crushing stage are primarily from smaller PFIs. The main evidence comes from

the excellent agreements between the 40 Ar/ 39 Ar ages of the inferred SFI gases and the late-stage hydrothermal event that was recorded by the crosscutting K-feldspar veins; and between the 40Ar/39Ar ages of the inferred PFI gases and the age of the host minerals dated using different methods (Bai et al., 2018; Xiao et al., 2019). This gas release pattern was further confirmed in a more recent study of multiple types of minerals from the Yaogangxian tungsten deposit where volatiles released from different stages of stepwise crushing and their corresponding ⁴⁰Ar/³⁹Ar geochronology were matched with the Raman gas compositions of different groups of SFIs and PFIs observed in the samples (Xiao et al., 2019). In general, we found that fluid inclusions with higher f values, larger volumes, and closer associations with micro-cracks are preferentially extracted. Based on these results, we proposed a detailed gas release pattern for most hydrothermal minerals from magmatichydrothermal systems which progresses from high-f inclusions, to larger liquid-rich SFIs along micro-cracks, to small liquid-rich PFIs. A final release of the tiny SFIs away from micro-cracks after the PFI degassing can be inferred from the increased amounts of SFI-associated gases such as CO₂, formamide, and ethane together with ³⁸Ar_{Cl} (Clderived argon) from the final several crushing steps of the cassiterite sample in Xiao et al. (2019). Based on this gas release pattern, higher-*f* fluid inclusions (especially those rich in CO_2), either secondary or primary, and microcrack-controlled SFIs with volumes larger than or similar to the PFIs would be extracted preferentially relative to the small, liquid-rich PFIs.

Because the experimental design used in this study is the same as in Xiao et al. (2019), the ore deposit and the studied hydrothermal minerals are also the same, it is safe to assume that similar gas release patterns apply to minerals analyzed in this study. Specifically, gases with enriched CO₂ and high CO₂/CH₄ ratios (>1) from the initial and even the intermediate crushing stages should correspond to the extraction of large SFIs-predominated fluid inclusion populations whereas those with enriched CH₄ and low CO₂/CH₄ ratios (<1) from the final crushing stage should correspond to the extraction of the small PFIs (Fig. 8). This view is confirmed by our Raman results, which indicate that the large SFIs are mainly (aquo) CO₂-rich with high Raman A(CO₂/CH₄) ratios whereas the relatively smaller PFIs are typically (aquo) methanoic with limited CO2 contents and very low Raman A(CO2/CH4) ratios. Gases released in the last several steps of the quartz sample 13YGX12Qtz and two cassiterite samples (13YGX05Cst and 13YGX17Cst) show increased CO_2/CH_4 ratios that are as high as those of the SFIs (Fig. 8b, h,i), which suggests breakup of the very fine SFIs in these crushing steps.

Fluid immiscibility occurred in quartz samples 13YGX07Qtz and 13YGX10Qtz, which resulted in different characteristics for the PFIs, i. e., the coexistence of (aquo) CO₂-rich and (aquo) CH₄-rich PFIs, whereas PFIs in wolframite, cassiterites, and other quartz samples (13YGX17Qtz and 13YGX28Qtz) are generally (aquo) methanoic (Table 1, as discussed Subsection 4.1). Based on the gas release pattern of Xiao et al. (2019), fluid inclusions with high vapor-filling degrees (low-density) are extracted earlier than the liquid-rich ones (high-density). This is further validated by the variation of water contents from very low values in the initial crushing stages to peak values in the later crushing stages during our stepwise crushing experiments (Fig. 9). Therefore, (aquo) CO₂-rich PFIs in the studied minerals that are generally larger and have higher vapor-filling degrees (e.g., Fig. 5d) should be preferentially extracted in the intermediate crushing stage. In contrast, smaller (aquo) methanoic PFIs (e.g., Fig. 5g,h) should be extracted much later.

5.2. Fluid origins and hydrothermal processes during mineralization

The remarkable compositional differences between the gases released from the SFIs and PFIs (Table B4, Figs. 8–11) indicate that postmineralization hydrothermal fluids are very different from mineralizing fluids. In the following subsections, along with S–H–O–C isotopes and liquid compositions of fluid inclusions, we discuss the potential source and evolution process of the ore-forming fluids based on the gas discrimination diagrams of $CO_2/CH_4-N_2/Ar$ of Norman and Moore (1999) and N₂–Ar–He of Norman and Musgrave (1994) (modified from Giggenbach (1986)).

5.2.1. Magmatic source of ore-forming materials

The W-Sn ore veins and the granites in the studied area are likely genetically associated given their close spatial relationship (Fig. 1b) and the overlap between the published ore-forming ages (163–153 Ma, Peng et al., 2006; Wang et al., 2010; Xiao et al., 2019; Deng et al., 2019; Li et al., 2020) and the crystallization ages of the granites (161–155 Ma, zircon U–Pb, Li et al., 2011, 2020).

As shown in Figs. 8–11 and Fig. A5, gases released from the PFIs in quartzs (samples 13YGX43Qtz and 13YGX12Qtz) from the granites are characterized by the enrichments of CH₄, N₂, and some other light hydrocarbons such as C_3H_8 and depletion of CO₂ with CO₂/CH₄ < 1. These compositional features are very similar to those of the smaller PFIs in the ore-bearing greisens and quartz veins, as exemplified by the crushing experiments of wolframite (sample 13YGX07Wlf), cassiterites (samples 13YGX05Cst and 13YGX17Cst), and quartzs (samples 13YGX10Qtz,

13YGX07Otz, 13YGX17Otz, and 13YGX28Otz) (Figs. 8-10, Fig. A5, Table B4). This similarity suggests that the magmatic-hydrothermal fluids that exsolved from the Yaogangxian granites might be the source of the mineralizing fluids. It is worth noting that the Yaogangxian granites are typical S-type granites derived from crustal anatexis (Chen, 1988; Li et al., 2015, 2020). C-O-H fluids could certainly form during devolatilization of hydrous phases (e.g., graphite) and C-bearing phases associated with the partial melting of metasedimentary rocks (Bartoli et al., 2013; Kadik et al., 2014). The relatively low oxygen fugacities of Jurassic W-Sn mineralization-related granites in South China ($Log f_{O2} =$ +1.51 to +5.68 (avg. +3.78) for W-related granites, $\text{Log}f_{\text{O2}}=+1.70$ to +3.22 (avg. +1.71) for W-Sn-related granites, and Log $f_{O2} = -5.32$ to +2.43 (avg. -0.83) for Sn-related granites, the Logf_{O2} values are relative to Ni-NiO buffer, Li et al., 2017b) would facilitate the generation of CH₄rich fluids via the reaction of $C + 2H_2O = CH_4 + O_2$ (Frost, 1979; Mysen et al., 2009).

Additional lines of evidence from the S-H isotopic data also point to a genetic link between the W-Sn mineralization and the Yaogangxian granitic magma. The observed sulfur isotope values (δ^{34} S) of ore mineral arsenopyrite and molybdenite vary from -0.2% to 1.4% (n = 7, Table B2), a range that is typical for a magmatic source (e.g., Moore and Fabbi, 1971; Sakai et al., 1982). The observed hydrogen isotopic compositions of methane (δD -CH₄ = -58‰ to -40‰, Table B3) are significantly enriched in deuterium relative to bacterial CH₄ (-400‰ to -150‰) and thermogenic CH₄ (-275‰ to -100‰) (Whiticar, 1999). Instead, these values are similar to those of magmatic CH₄ (-150‰ to -50‰, Whiticar, 1999; Potter and Longstaffe, 2007), which suggests a dominant magmatic origin of the methane hydrogen. These findings are consistent with previously published results of S-Pb isotopes on sulfides and H-O isotopes on wolframites and quartzs (Zhang, 1987; Zhu et al., 2014; Li et al., 2017a), all of which are consistent with a magmatic origin for the mineralizing fluids.

Magmatic differentiation can greatly concentrate tungsten and tin into the residual melt (Mustard et al., 2006; Hulsbosch et al., 2016). This process could also lead to high tungsten and tin concentrations in the exsolved magmatic-hydrothermal fluids, which could therefore be a significant reservoir of ore-forming materials in the studied deposit.

5.2.2. Insignificant contribution of meteoric water to W-Sn mineralization

Previous He–Ar isotopic studies performed on fluid inclusions of chalcopyrite, wolframite, pyrite, and arsenopyrite in the deposit (Chen et al., 2011; Hu et al., 2012) yielded ³He/⁴He ratios (0.05–3.03 Ra) ranging between those of typical crustal fluids (0.01–0.05 Ra, Mamyrin and Tolstikhin, 1984; Turner et al., 1993) and the sub-continental mantle (~6 Ra, Dunai and Baur, 1995; Gautheron and Moreira, 2002). Their ⁴⁰Ar/³⁶Ar ratios (325–1191) are generally higher than the atmosphere (295.5, Nier, 1950). Their ⁴⁰Ar*/⁴He values are lower than both crustal and mantle values. These data led many authors to propose that fluid mixing between magmatic water and meteoric water governs the precipitation of W-Sn minerals (Chen et al., 2011; Hu et al., 2012).

The geochemical characteristics of fluid inclusions from similar oreminerals reported here, however, indicate that the contribution of meteoric water is unnecessary for mineralization. Gases from the PFIs (corresponding to gases released during the final crushing stage) in the studied ore/gangue minerals from ore-bearing veins yielded relatively high N₂/Ar ratios (327-861 for cassiterite, 474-713 for wolframite, and 60.7-469, 115-337, and 386-943 for guartzs from the guartz veins, greisen and greisen-bordered quartz vein, respectively, Table B4) and low CO₂/CH₄ ratios (<1), which are distinct from typical shallow meteoric fluids that have much lower N2/Ar ratios (~38, Norman and Musgrave, 1994) and higher CO₂/CH₄ ratios (Fig. 11b–f). This is in line with the O isotopes of fluids (δ^{18} O-H₂O = 3.9–5.1‰) in quartzs from ore-bearing veins. Even if there might be a potential underestimation of the calculated δ^{18} O values using fluid inclusion homogenization temperatures, these data still fall close to the field of magmatic water and away from the meteoric water line (Fig. 13a). On the other hand, gases



Fig. 13. Isotopic compositions of quartz samples from ore-bearing veins. (a) Plot of δ^{18} O-H₂O versus δ D-H₂O values. The fields of magmatic and metamorphic waters are from Taylor (1997) and Ohmoto (1986). The field of organic water is revised after Sheppard (1986). The field of coaly sediments is from Polya et al. (2000) and Smith et al. (1985). The meteoric water line is from Craig (1961). Previous published H–O isotopic compositions of vein quartzs are from Zhu et al., (2014) and Li et al., (2017a). (b) Plot of δ D-CH₄ versus δ^{13} C-CH₄ values, with the template from Potter et al. (2013). The fields of bacterial and thermogenic methane are modified after Schoell (1988). The field of mantle/magmatic methane is inferred from Whiticar (1999) and Welhan and Craig (1983).

from the SFIs (corresponding to gases extracted during the initial crushing steps) in several samples, such as quartz samples 13YGX10Qtz and 13YGX17Qtz (Fig. 11b,e), have N₂/Ar and CO₂/CH₄ ratios that fall among evolved magmatic water, shallow meteoric water, and evolved crustal water, i.e., meteoric water in equilibrium with crustal rocks (Norman and Moore, 1999). These features collectively suggest that the meteoric water likely only participated in the formation of SFIs rather than the W-Sn mineralization. This study showcases how stepwise crushing technique can improve our understanding of the ore-forming process by allowing us to distinguish gases from SFIs and PFIs. This is a difficult task for other extraction techniques, such as decrepitation, because SFIs and PFIs can have similar decrepitation temperatures. For example, the partial overlap of T_h values between PFIs and SFIs in the studied quartz samples (Fig. 7e) indicates that using decrepitation techniques would not be able to effectively separate the gases released from SFIs and PFIs.

5.2.3. Crustal components in the mineralizing fluids

Although mineralization-related granites are typical S-type granites of crustal origin, results of the crushing experiments suggest contributions of additional crustal-derived fluids to the W-Sn mineralization. In the N₂/Ar-CO₂/CH₄ discrimination diagrams, data points associated with the bulk PFIs of ore/gangue minerals approach the field of organic water, with some data falling near the field of evolved crustal water (e. g., Fig. 11b, e,f), which is different from the magmatic-hydrothermal fluids derived from the Yaogangxian S-type granites (defined as the Yaogangxian magmatic-hydrothermal fluids) that plot between the fields of organic water and evolved magmatic water (Fig. 11a). In the N2-Ar-He ternary plots, gases released from the PFIs in ore mineral wolframite all fall within the field of non-magmatic crustal water (Fig. 12) whereas the Yaogangxian magmatic-hydrothermal fluids fall between the fields of non-magmatic crustal water and traditional magmatic water (Fig. A6). This attests to additional crustal-derived components in the ore-forming fluids. Additionally, exsolved magmatic-hydrothermal fluids are generally Ca-poor and F-rich (Barton, 1987; Webster et al., 2004; Thomas et al., 2005; Harlaux et al., 2017) with F^{-}/Cl^{-} ratios > 1 (Zhang, 1992). Those exsolved from S-type granites also have K^+/Na^+ ratios > 1 (Zhang, 1992; Hulsbosch et al., 2016). However, fluids in quartzs from ore-bearing veins are characterized by high Ca^{2+} , low to negligible F⁻ contents, and low K⁺/Na⁺ (0.21–0.32) ratios < 1 (Table B5 in Appendix B). These fluids are distinct from the exsolved magmatic-hydrothermal fluids but similar to the deep groundwater that is characterized by high Ca^{2+} contents with Na^+/K^+

ratios > 1 (Iwatsuki and Yoshida, 1999; Jeong, 2001) and F⁻/Cl⁻ ratios \ll 1 (Zhang, 1992). These compositions indicate chemical exchanges between the exsolved magmatic-hydrothermal fluids from the Yao-gangxian granites and the non-magmatic crustal fluids in equilibrium with the metasedimentary wall rocks.

5.2.4. Fluid-rock interactions during mineralization

Given the relatively uniform liquid compositions of fluid inclusions in quartz samples from ore-bearing veins (Table B5), e.g., Cl⁻/Na⁺ (6.50–11.27), Cl⁻/Ca²⁺ (3.93–7.90), SO₄²⁻/Na⁺ (1.38–2.25), and SO₄²⁻/Ca²⁺ (0.86–1.57) ratios, the presence of both magmatic and nonmagmatic crustal components in ore-forming fluids is unlikely caused by fluid mixing between the Yaogangxian magmatic-hydrothermal fluids and organic-matter-bearing non-magmatic crustal fluids. This is further supported by the observed (Fig. 7) and published (Cao et al., 2009; Dong et al., 2011; Li et al., 2017a) *T*_h and salinities of fluid inclusions in ore minerals from this deposit, which are widely scattered without discernible linear correlations.

Instead, chemical exchange between the exsolved magmatichydrothermal fluids and organic-matter-bearing sedimentary wall rocks could generate the characteristics observed in the studied PFIs. The low \deltaD-H₂O values of fluids in quartz samples from ore-bearing quartz veins that extend from the field of magmatic water towards the field of organic water or coaly sediments in the diagram of \deltaD-H₂O versus δ^{18} O-H₂O (Fig. 13a), which is also consistent with different degrees of fluid-rock interactions in the studied deposit. The absence of any correlation between the SFI proportions and the δD -H₂O values among the analyzed samples (Fig. A7 in Appendix A) indicates negligible influence from SFIs on the δD -H₂O values. Instead, many studies have suggested that fluid-rock interaction is an effective mechanism to lower the hydrogen isotopes of water which could result in a wide range of hydrogen isotope compositions (Taylor, 1977; Harris et al., 2005). For example, hydrogen exchange during fluid-rock interactions with organic materials (Charef and Sheppard, 1987; Munoz et al., 1994) and coaly sediments (Polya et al., 2000) has been shown to effectively drive water hydrogen isotopes to lower values approaching that of organic water.

Additionally, in the δ^{13} C-CH₄ versus δ D-CH₄ binary diagram of Schoell (1980, 1988), fluid-rock reactions can be identified by the "decoupling" of hydrogen and carbon isotopes of CH₄. Even though hydrogen isotopes of CH₄ in quartz samples from ore-bearing veins are similar to those of magmatic methane, the carbon isotopes of CH₄ in the same quartz samples (-41.7% to -39.4%, Xiao et al., 2019) are more depleted than those of magmatic methane (Fig. 13b). Instead, these

relatively low δ^{13} C-CH₄ values are similar to those of methane produced by high-temperature inorganic chemical reactions (-53.6% to -19.1%); Horita and Berndt, 1999; Mccollom and Seewald, 2006; Taran et al., 2007), which suggests that they are of abiogenic origin and likely formed by fluid-rock interactions. Abiogenic formation via Fischer--Tropsch-type (F-T-t) reactions can lead to ¹³C- and D-depletion in the generated CH₄ and sometimes even drive the isotopic compositions to the field of thermogenic gas (Potter et al., 2013). However, such effect on the hydrogen isotope system can be limited. For example, CH₄ generated by abiogenic Fischer-Tropsch synthesis from initial magmatic CO2 in the Baogutu porphyry copper deposit, NW-China, has δD -CH4 values that vary from -108.0% to -59.5% (avg. -87.9%, Cao et al., 2014) which still fall within the range of magmatic origin. Therefore, fluid-rock interactions could have driven the carbon isotopes of CH₄ to lower values whereas its hydrogen isotopes remained similar to those of the magmatic methane, which is consistent with the results shown in Fig. 13b.

5.3. W-Sn Metallogenic mechanism of the Yaogangxian tungsten deposit

5.3.1. Fluid-rock interaction is an effective mechanism promoting W-Sn mineralization

It has been well documented that fluid-rock interaction is one of the major mechanisms for W-Sn mineralization, which is also common in vein-type W-Sn deposits (Polya et al., 2000; Chicharro et al., 2016). Metasedimentary wall rocks can provide Fe and sometimes Mn for wolframite precipitation through fluid-rock interaction processes (Eugster, 1985; Lecumberri-Sanchez et al., 2017). Fluid-rock interactions can also change the physical and chemical conditions of the fluids, such as pH values, which promotes W-Sn precipitation.

Below 400 °C, tungsten is mainly transported as alkali tungstate ion pairs, halide complex, $H_2WO_4^0$, HWO_4^- , WO_4^{2-} , carbonate complexes, as well polymeric tungstates (Heinrich, 1990; Wood and Samson, 2000). The increase in pH will greatly promote tungsten precipitation from a moderate-temperature fluid by destabilizing both monomeric tungstate species and polymeric tungstates (Higgins, 1985; Wood and Samson, 2000; Wang et al., 2020). Acid neutralization is an important mechanism for cassiterite precipitation from a W-Sn-bearing fluid (Heinrich, 1990). Fluid-rock interactions can reduce oxidized carbon species (CO₂, CO, HCO₃ or other inorganic carbon species) to produce CH₄ (Horita and Berndt, 1999; Mccollom and Seewald, 2006; Taran et al., 2007). The loss of CO_2 or HCO_3^- from the hydrothermal fluid would increase the pH, which in turn promotes the precipitation of wolframite (Higgins, 1985). If the wall rocks contain carbonate, acid neutralization could happen through the reaction of $SnCl_2 + CaCO_3 + H_2O \rightarrow SnO_2 + CaCl_2 + CO_2 +$ H₂ (Eugster, 1985), which could promote cassiterite formation. Additionally, the iron-rich country rocks or carbon-bearing metasediments can act as catalysts that promote the interactions between fluid and wall rocks (Su et al., 2009).

In the investigated deposit, the ore-forming materials were most likely sourced from the Yaogangxian magmatic-hydrothermal fluids as discussed in Subsection 5.2.1. Highly evolved granitic magma generally exsolve fluorine-rich fluids during late-stage crystallization (Pollard et al., 1987; Thomas et al., 2005; Harlaux et al., 2017). Previous chemical analyses suggested that the Yaogangxian granites contain high fluorine with contents up to 6100 ppm (Chen, 1992). The presence of fluorites in the granites (Lin et al., 1986) and the ore-bearing veins (Fig. A2) indicates that exsolved magmatic-hydrothermal fluids in this deposit were enriched in fluorine. Fluorine enrichment in fluid typically requires low Fe concentrations in the late-stage magmatic fluids (Barton, 1987; Lecumberri-Sanchez et al., 2017). However, iron is a crucial element for wolframite formation, especially for ferberite. Therefore, an external iron source is required. In the Yaogangxian deposit, the wall rocks are Cambrian and/or Devonian metasedimentary strata (Chen, 1981, 1992; Lin et al., 1986), which should contain abundant iron, as evidenced by the presence of micas in the meta-sandstone (see

Subsection 2.1), and strong greisenization and pyritization wall-rock alterations (Fig. A1). Even coal-bearing layers are locally present (Chen, 1992; Zhu et al., 2015), which indicates high carbon contents in the wall rocks. Interactions between the carbon phases bearing reduced magmatic-hydrothermal fluids and the Fe-bearing and C-rich meta-sedimentary wall rocks could be an effective mechanism for W-Sn deposition, as the wall rocks could provide not only the catalysts that promote fluid-rock interactions but also Fe and/or Mn for wolframite precipitation (Lecumberri-Sanchez et al., 2017).

Additionally, the high Ca^{2+} concentrations and low K^+/Na^+ (0.21–0.32) ratios < 1 (Table B5) of fluids in quartz samples are the best evidence that fluid-rock interactions had occurred in the deposit and introduced Ca^{2+} and Na^+ from the metasedimentary wall rocks into the hydrothermal fluids. Moreover, the increase in pH values as a result of fluid-rock interactions could be a much more effective mechanism for wolframite precipitation than the simple cooling process of magmatic-hydrothermal fluids (Higgins, 1985).

5.3.2. The role of fluid immiscibility on W-Sn mineralization

It has been suggested that CO₂-involved phase separation such as fluid immiscibility can cause abrupt changes in fluid chemistry, which is considered an important mechanism of W-Sn metal precipitation (e.g., Higgins, 1985; Mohamed, 2011). Fluid immiscibility has also been suggested as a potential mechanism for ore formation in the investigated deposit (Yu et al., 2015). To assess its impact on ore formation, we reconstructed the hydrothermal process of the Yaogangxian vein-type tungsten deposit below.

Microthermometric results show that the major $T_{\rm h}$ peaks of cassiterite, wolframite, and quartz migrate toward lower temperatures (Fig. 7c), which indicates that these minerals precipitated sequentially as the ore-forming fluid cooled. Characteristics of PFIs in earlier-formed ore minerals cassiterite and wolframite are different from those of PFIs in spatially associated but later-formed quartz. Microscopic observations coupled with Raman analytical results suggest that CO2-rich two- and tri-phase fluid inclusions are absent in PFIs in cassiterite (Fig. 4) while only minor CO2-rich two-phase PFIs are observed in wolframite as suggested by the occurrence of clathrates during cooling of the fluid inclusions (Table B1), which indicates a gradual increase of CO₂ with the evolution and cooling of the ore-forming fluids. In contrast, CO₂-rich two- and tri-phase PFIs are common in quartz samples associated with minor ore minerals or abundant chalcopyrite (Fig. A4). The presence of multiple sulfides is usually a sign of later formation in W-Sn deposits (e. g., Fig. 3d) as the ore-forming temperature (above 300 °C) is generally too high for base metal sulfide precipitation (Audétat et al., 2000b; Bodnar et al., 2014). Above mentioned fluid inclusion characteristics of later-formed quartzs are consistent with phase separation due to fluid immiscibility. As this process is absent in PFIs from earlier-formed ore minerals cassiterite and wolframite, fluid immiscibility most likely occurred at a cooler temperature at the end of or after the W-Sn mineralization and thus played limited roles on W-Sn mineralization in the investigated deposit.

Fluid inclusions in late-stage minerals could trap heterogeneous fluids as homogeneous ore-forming fluids intersect the solvus during cooling leading to fluid immiscibility (Diamond, 1994). Continuous fluid-rock interactions could also introduce Ca^{2+} from metasedimentary wall rocks and add CH₄ into the fluids to decrease the solubility of the non-polar gases in the liquid phase (salting-out effect, Liebscher, 2007) and to expand the two-phase field (Naden and Shepherd, 1989; Liebscher, 2007), which might facilitate the final phase separation.

5.4. A perspective on the fluid evolution in the Yaogangxian tungsten deposit

Detailed petrography, microthermometry, and gas/liquid compositions of fluid inclusions and the isotopic evidence discussed above allowed us to rebuild the fluid evolution history of the W-Sn mineralization of the Yaogangxian deposit (see Fig. 14).

The CH₄-rich reduced magmatic-hydrothermal fluids that exsolved from the highly evolved Yaogangxian granitic magma, which contain high concentrations of ore-forming elements, e.g., W and Sn, are significant components in the ore-forming fluids (Fig. 14). These fluids interacted with the metasedimentary wall rocks and generated mineralizing fluids with low CO₂/CH₄ ratios (Fig. 8) and hydrocarbon species (Fig. A5) that resemble the exsolved Yaogangxian magmatichydrothermal fluids. But they are more enriched in CH₄, light hydrocarbons such as C₃H₈, Ca²⁺ and Na⁺ (Table B5). Non-magmatic crustal He and N₂ could be introduced into such ore-bearing fluids as well (Fig. 14). Interactions with carbonate-rich wall rocks did not affect S isotopic system of ore minerals and the H isotopes of CH₄, however, it lowered the H isotopes of water and C isotopes of CH₄ significantly. Precipitation of wolframite and cassiterite could happen soon after the fluid-rock interaction process that led to the increase of the fluid pH values and the reducibility of the fluids. Towards the end of ore formation, fluid cooling coupled with the addition of Ca²⁺ and CH₄ derived from fluid-rock interactions triggered fluid immiscibility and caused phase separations (e.g., Fig. 5d). As a consequence, the CH_4 -rich mineralizing fluids could eventually evolve into CO₂ + CH₄ carbonic vapors and a CH₄- and H₂O-rich but CO₂-depleted residual phase, all of which could be simultaneously trapped in later-formed quartzs (e.g., Fig. 5c,d). On the other hand, structurally controlled micro-cracks could capture gases released from various sources as CO2-rich SFIs form.

6. Conclusions

Volatiles captured in both primary and secondary fluid inclusions in ore minerals and quartzs from ore veins of the Yaogangxian tungsten deposit as well as its associated granites were progressively extracted and analyzed using a quadrupole mass spectrometer coupled with a stepwise *in vacuo* crushing apparatus. Combining this novel approach with traditional Raman spectroscopic and S–H–O–C isotopic analyses, our data have shed light on the nature and origin of the mineralizing fluids, the mechanism for W-Sn precipitation as well as the evolution of the fluids from this deposit. The main pieces of the conclusions are summarized below.

- Detailed microscopic observations revealed two main generations of fluid inclusions in minerals, i.e., larger, irregular SFIs along microcracks with various vapor-filling degrees and smaller, regular, liquid-rich PFIs in three-dimensional clusters or along mineral growth zones.
- 2) Raman spectroscopic results coupled with QMS analyses revealed that gases derived from the PFIs, i.e., the mineralizing fluids, are CH₄-rich with lower CO_2/CH_4 ratios (<1) and higher C_3H_8 contents compared with gases derived from the SFIs, i.e., the post-mineralization fluids, which are CO_2 -rich oxidized fluids with high CO_2/CH_4 ratios.
- 3) Gases from the PFIs in quartzs from the Yaogangxian granite and in ore/quartz minerals from ore-bearing greisens and quartz veins show compositional similarities, such as enrichments of CH₄, N₂, and C₃H₈, depletion of CO₂ and C₄H₁₀, similar species of organic gases, as



Fig. 14. Schematic fluid evolution in the Yaogangxian tungsten deposit. See text for detailed explanations.

well as low CO_2/CH_4 (<1) and high N_2/Ar (60.7–943) ratios. Along with their magmatic sulfur and methane hydrogen isotopic compositions, these results collectively point to a magmatic source for the ore-bearing fluids.

- 4) Gases from the PFIs in ore mineral wolframite show high crustal-like He contents in the N₂–Ar–He ternary diagrams. Fluids in quartz samples also have non-magmatic crustal-like high Ca²⁺, low F⁻ concentrations, and low K⁺/Na⁺ ratios (<1). These characteristics are distinct from those of the magmatic-hydrothermal fluids derived from the Yaogangxian S-type granites, which indicates additional fluid input from crustal components. Combined with the relatively low fluid H and methane C isotopes of the quartz samples from orebearing veins, these results indicate that fluid-rock interactions occurred during mineralization.
- 5) Detailed microthermometry of fluid inclusions suggests that gangue mineral quartz generally form later than ore minerals cassiterite and wolframite. Compared with the associated ore minerals, PFIs in some quartz samples show much larger variabilities of vapor-filling degrees, gas compositions, and microthermometry which can be attributed to fluid immiscibility.
- 6) Base on the petrography, microthermometry, and gas/liquid compositions of fluid inclusions as well as S–H–O–C isotopes, we propose that exsolved magmatic-hydrothermal fluids interacted with the metasedimentary wall rocks and this fluid-rock interaction processs promoted W-Sn precipitation in the Yaogangxian tungsten deposit. Intensified fluid-rock interaction processes, along with fluid cooling, likely induced fluid immiscibility at the end of mineralization. However, contrary to popular belief, fluid immiscibility and CO₂-rich fluids may have only played limited roles in W-Sn mineralization of the Yaogangxian tungsten deposit.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

The geochemical data and supplementary figures of this study are included in the appendixes. Datasets related to this article can be found in the Pangaea data repository at https://doi.pangaea.de/10.1594/PANGAEA.925167.

Appendix A. Supplementary data

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