Ore Geology Reviews 65 (2015) 55–69

Contents lists available at ScienceDirect

Ore Geology Reviews

journal homepage: www.elsevier.com/locate/oregeorev

Infrared microthermometric and noble gas isotope study of fluid inclusions in ore minerals at the Woxi orogenic Au–Sb–W deposit, western Hunan, South China

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ARTICLE INFO

Article history:
Received 2 March 2014
Received in revised form 11 August 2014
Accepted 12 August 2014
Available online 16 September 2014

Keywords:
Fluid inclusions
Noble gas isotope
Ore minerals
Orogenic Au–Sb–W deposit

ABSTRACT

The Woxi Au–Sb–W deposit, hosted by the Neoproterozoic low-grade metamorphic clastic rocks, is located in a brittle-ductile shear zone within the Xuefengshan Range, South China. Orebodies are predominantly banded quartz veins, which are strictly controlled by bedding faults and display significant vertical extents (up to 2 km) without obvious vertical metal zoning. Fluid inclusions hosted in quartz, scheelite, and stibnite from quartz–scheelite and quartz–sulfide–gold veins have been studied using conventional and infrared microscopy, respectively. Four types of fluid inclusions were identified based on petrography, including type I (two-phase, liquid-rich aqueous inclusions), type II (two- or three-phase, CO_2-rich inclusions), type III (two-phase, vapour-rich aqueous inclusions), and type IV (single-phase aqueous inclusions). The fluid inclusions in ore minerals (scheelite and stibnite) and their coexisting quartz largely share similar characteristics in terms of their types, homogenization temperatures and salinities. This is consistent with the fact that these ore minerals are always intergrown with quartz. Microthermometric and laser Raman data indicate a low-to-moderate temperature (140–240 °C), low salinity (<7.0 wt.% NaCl equiv.), CO_2-rich, N_2-bearing aqueous ore-forming fluid. Such fluid is further identified as a deeply non-magmatic crustal fluid rather than a mantle-source fluid by the significantly low $^3He/^4He$ ratios (0.002–0.281 Ra), and a small amount of meteoric water or host-rock-buffered fluid could be involved. W ore precipitation was probably associated with mixing between a deeply-originated crustal fluid and host-rock-buffered fluid based on the fluid inclusion features in scheelite and quartz-I. However, Au and Sb ore deposition probably resulted from boiling which was caused by the marked pressure drop. Geological features (such as banded structure and crack-sealing structure) also indicate that fluid pressure fluctuation induced by fault-valve mechanism occurred during ore precipitation. These characteristics of the ore-forming fluids in the Woxi deposit are in good agreement with the definition of orogenic gold deposits and the Woxi Au–Sb–W deposit is probably an atypical orogenic gold deposit for its unique ore-forming element association.

1. Introduction

The physico-chemical properties of fluids and solids trapped in ore minerals and coeval gangue minerals provide key information about controls on metal deposition in ore deposits. Although a few metallic minerals such as scheelite and some sphalerite are transparent, most are opaque under the traditional transmitted-light microscope. Thus, in the past several decades, fluid inclusions were usually studied only within transparent gangue minerals, and their microthermometric data were extrapolated to the coexisting ore minerals. With the application of infrared microscopy in earth sciences in recent years, fluid inclusions in some opaque ore minerals, e.g. wolframite (Bailly et al., 2002; Campbell et al., 1984; Lüders, 1996; Wei et al., 2012), stibnite (Bailly et al., 2000; Buchholz et al., 2007; Hagemann and Lüders, 2003; Lüders, 1996), and pyrite (Kouzmanov et al., 2010; Lindaas et al., 2002; Lüders and Ziemann, 1999; Zhu et al., 2013), can be directly observed and analysed, revealing that different homogenization temperatures and salinities probably exist between the spatially associated gangue and ore minerals in some hydrothermal deposits (e.g. Bailly et al., 2000; Campbell and Panter, 1990; Wang et al., 2013; Wei et al., 2012), even for those documented cases where unambiguous textural evidence demonstrates a clear coeval timing between gangue and ore minerals (Campbell and Robinson-Cook, 1987; Giamello et al., 1992). Thus, examining fluid inclusions in ore minerals is crucial; it can

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http://dx.doi.org/10.1016/j.oregeorev.2014.08.014

preclude any doubt whether fluid inclusions studied in gangue minerals adequately reflect the ore-forming fluids from which ore minerals precipitated.

Gold-only lode deposits are genetically associated with low salinity (typically <6 wt.% NaCl equiv.) aqueous, CO_2-bearing fluid inclusions similar to fluids generated during transitional sub-greenschist to amphibolite facies metamorphism of altered volcanosedimentary rocks (Goldfarb et al., 2005; Groves et al., 1998; Kerrich et al., 2000; Tomkins, 2013). These deposits are found from the Archean to recent orogenic belts (Chen et al., 2012a; de Boorder, 2012; Goldfarb et al., 2001; Hronsky et al., 2012; Zachariáš et al., 2013), and considered to be an inherent part of an orogeny (Fu et al., 2012; Groves et al., 2005). Lode gold deposits are widespread in the Precambrian low-grade metamorphic clastic rocks throughout the Xuefengshan Range, western Hunan, South China, and are also considered to be orogenic deposits (Chen, 2006; Zhou et al., 2002). However, compared to typical orogenic "gold-only" ore deposits, the ore-forming element associations for these gold deposits are unique, predominated by Au–Sb–W, Au–W, and Au–Sb. As the largest gold deposit occurred in the Xuefengshan Range, the Woxi Au–Sb–W deposit is representative of these unique metal association gold deposits in this region, it provides an important natural laboratory for investigating the nature and source of ore-forming fluid of lode gold deposits in the Xuefengshan Range.

Few systematic fluid inclusion studies on ore minerals (especially opaque ore minerals) have been performed on the Woxi Au–Sb–W deposit, although many genetic opinions have been proposed for this deposit, including (1) sedimentary exhalative (SEDEX) origin (Gu et al., 2007, 2012; Zhang, 1985), (2) magmatic hydrothermal origin (Mao and Li, 1997; Peng and Frei, 2004), and (3) metamorphic hydrothermal origin (Luo et al., 1984; Yang, 1992). In this study, fluid inclusions hosted in scheelite and stibnite, as the most important ore minerals in different ore-forming stages, are examined. For comparison, fluid inclusions in their coexisting quartz are also studied. In addition, noble gas isotope data on ore minerals are determined, for the purpose of tracing possible fluid sources and mineralization processes of the ore-forming fluids (e.g. Burgess et al., 1992; Kendrick et al., 2011; Landis and Hofstra, 2012; Li et al., 2011; Zeng et al., 2014). The objectives of this paper are: (1) to decipher the nature and sources of the fluids involved in the formation of gold, antimony and tungsten ores in the Woxi deposit; (2) to determine the characteristics of the hydrothermal fluids responsible for gold, stibnite, and/or scheelite deposition in the Xuefengshan Range on the basis of fluid inclusion data obtained in this study and previous studies; and (3) to give some new genetic constraints for the Woxi deposit.

2. Regional geology

The Xuefengshan Range in western Hunan, South China, is located between the Yangtze Block and the Cathaysia Block (Fig. 1). It consists mainly of the Mesoproterozoic Lengjiaxi Group and Neoproterozoic Banxi Group (HBGMR, 1988). The Lengjiaxi Group is composed of flysch-type sedimentary rocks, including marine clastic rocks intercalated with lava flows. The Banxi Group consists of flyschoid-type clastic rocks and argillite. All the Proterozoic strata were extensively deformed and metamorphosed to sub-greenschist facies during regional metamorphism at ~1000 and ~800 Ma (HBGMR, 1988). The cover sequence includes Sinian and Cambrian strata, with minor Ordovician and Silurian strata. Recent studies suggest that the Xuefengshan Range was involved in the early Paleozoic and early Mesozoic intracontinental orogens, recorded by magmatism, folding, faulting and metamorphic deformation (Chu et al., 2012; Li et al., 2009; Zhang et al., 2013). In addition, compared to the eastern Xuefengshan Range, magmatic activity in the western part is relatively scarce.

Lode gold deposits are widespread throughout the Xuefengshan Range. Gold mineralization usually occurs in the Proterozoic, Sinian and Cambrian low-grade metamorphic clastic rocks, and has metal

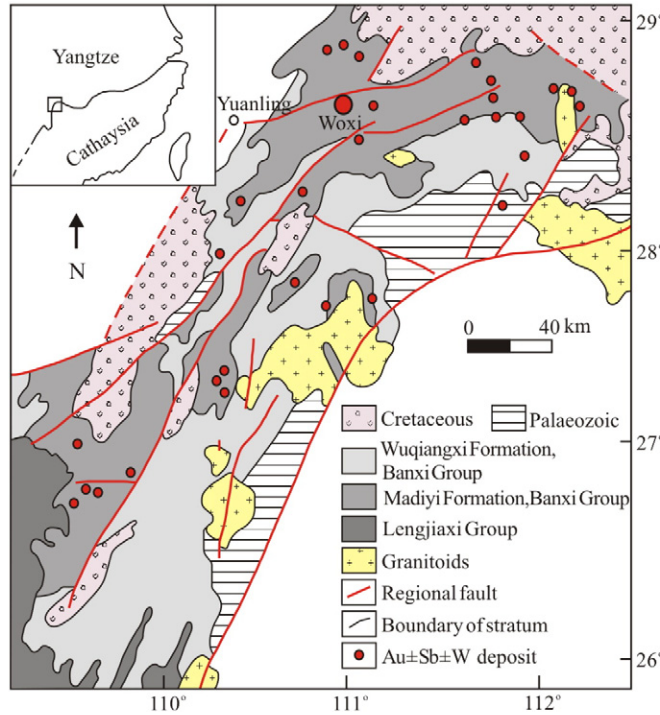


Fig. 1. Geological sketch map of the Xuefengshan Range in western Hunan, China (modified after Peng and Frei, 2004).

associations of Au–(Sb–W). For example, the Woxi Au–Sb–W deposit (Peng and Frei, 2004; Peng et al., 2003a), the Fuzhuxi and Xichong Au–Sb deposits (Yao and Zhu, 1993), the Xi'an Au–W deposit, and the Mobin and Herenping Au deposits. The Woxi deposit is the largest gold deposit in the Xuefengshan Range and displays a unique Au–Sb–W metal association.

3. Ore deposit geology

The Woxi Au–Sb–W deposit is located in the Xuefengshan Range in western Hunan, South China (Fig. 1). It was discovered in 1875, and mining began in 1895. The Au, Sb, and WO_3 metal reserves for the Woxi deposit amount to >50, 220,000, and 25,000 t, and the average grades of Au, Sb, and W in the ores are 9.77 ppm, 2.84%, and 0.3%, respectively. In general, the metal minerals display an obvious lateral zoning, ranging from W–Au in the east, to W–Sb–Au in the middle, and Sb–Au in the west, accompanying tungsten mineral phase from scheelite to wolframite (GHCPAPF, 1996).

The strata exposed in the Woxi region mainly consist of the Proterozoic Lengjiaxi Group and Banxi Group (Fig. 2). The latter, which is a series of flyschoid consisting of slate and phyllite interbedded with local volcanic materials, can be subdivided into the Madiyi Formation and the Wuqiangxi Formation. The Wuqiangxi Formation concordantly overlies the Madiyi Formation, and the latter discordantly overlies the Lengjiaxi Group (Luo et al., 1984). The lithologic sequence of the Madiyi Formation consists of low-grade metamorphic purple-red sericite slate, sandstone slate, and calcareous sericitic slate; orebodies in this deposit are restricted within the purple-red calcareous sericitic slate in the middle Madiyi Formation, and controlled by interlay faults (Fig. 2A–B). No magmatic activities are preserved in the mining district or adjacent regions (Fig. 2A).

Orebodies in the Woxi mining district are predominantly composed of quartz veins, which occur in the footwall of the E–W striking Woxi Fault (GHCPAPF, 1996). These quartz veins can be divided into banded vein, network vein (or veinlet), and discordant vein (e.g. Fig. 3A–C; Luo et al., 1984; Gu et al., 2007). Economically, the banded veins rank as the most important, contributing about 70% of the metal

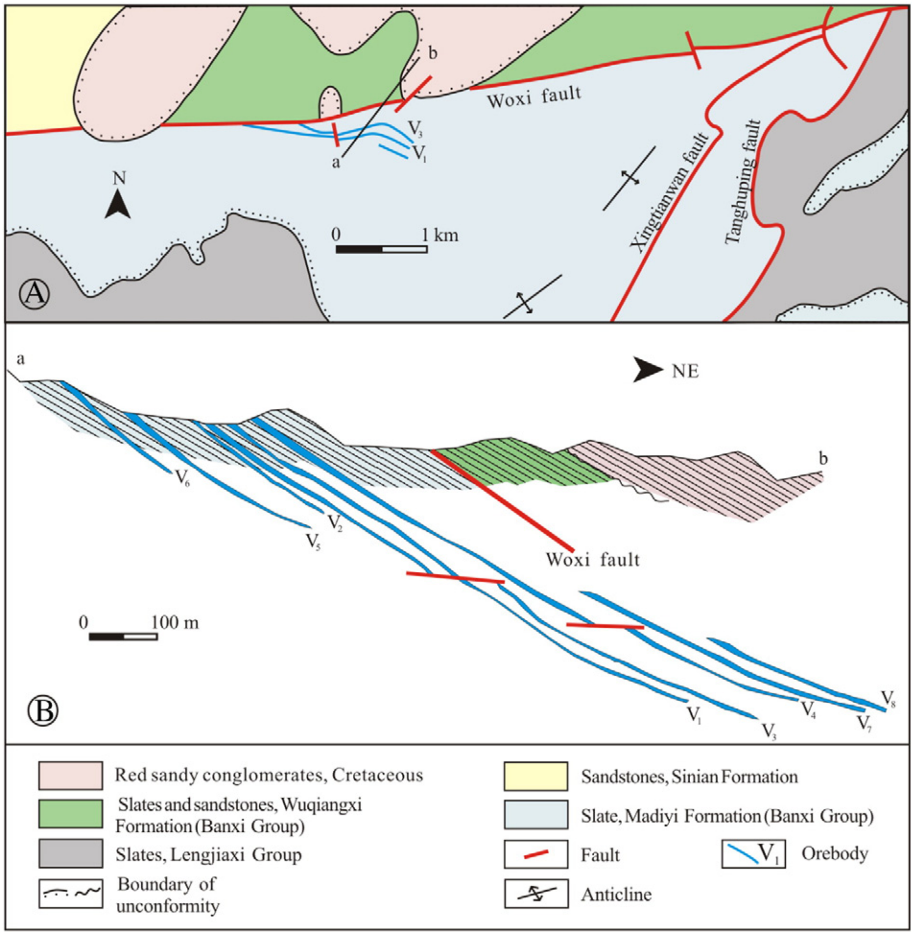


Fig. 2. Sketch map of the Woxi deposit district (modified after GHCPAPF, 1996). (A) Geological map; (B) Cross section a-b (marked in A) through the Woxi deposit.

accumulations for this deposit (Luo et al., 1984). They are E–W striking, gentle dipping (~20°–30°), with significant vertical extents (up to 2 km) and without obvious vertical metal zoning.

These gently-dipping veins are commonly parallel to the host strata and the Woxi Fault (Fig. 2B), and display open-space filling textures (Fig. 3D–E), containing brecciated vein fragments (Fig. 3D) or wall rocks (Fig. 3E). Boudinage and folding of some veins are also observed (Fig. 3F; Li et al., 1983; Liu, 1992), reflecting their pre-kinematic to, more commonly, syn-kinematic timing. The alteration halo around these ore veins in clastic sedimentary rocks is distinguished as widespread silicification, pyritization, carbonatization and sericitization.

Metallic minerals are dominated by scheelite (Fig. 4A), pyrite (Fig. 4B–E), stibnite (Fig. 4C–F), native gold (Fig. 4G–H) and locally wolframite, with minor arsenopyrite, sphalerite, and galena; the gangue minerals include quartz (Fig. 4A–H) and minor amounts of sericite, carbonate, and chlorite (GHCPAPF, 1996). Detailed mineralogical features have been previously documented (GHCPAPF, 1996; Liang and Zhang, 1986; Shao et al., 1996; Zhang et al., 1996) and the mineral paragenesis for the Woxi deposit was divided into the quartz–carbonate stage, quartz–scheelite stage, quartz–sulfide–gold stage, and quartz–carbonate stage (GHCPAPF, 1996; Liang et al., 1981; Liu, 1992). Features of each stage are summarized in Fig. 5.

The early quartz–carbonate stage is barren with no discernible wall rock alteration zones present (GHCPAPF, 1996).

The quartz–scheelite stage consists mainly of massive quartz (Fig. 4A, C) with scheelite (Fig. 4A), wolframite, carbonate, apatite, minor arsenopyrite and siderite. Wolframite is less abundant than scheelite and usually occurs in the western mining area (GHCPAPF, 1996; Zhu et al., 2014). Scheelite occurs as irregularly shaped and massive aggregates in quartz veins, commonly cut by the later quartz veinlets containing pyrite, stibnite, or native gold (Fig. 4A). Quartz, the most abundant mineral, mainly appears as subhedral–anhedral grains and is commonly brecciated (Fig. 4A, C, D, E).

The quartz–sulfide–gold stage is characterized by the widespread occurrence of pyrite (Fig. 4B–E), stibnite (Fig. 4C–E), and native gold (Fig. 4G–H), with minor arsenopyrite, sphalerite, galena, and sulfosalt minerals. The earlier quartz–scheelite ore fragments sometimes occur in the quartz–sulfide–gold veins (Fig. 3D, 4D–4E). Pyrite is the most abundant gold-bearing mineral in these veins, followed by stibnite, scheelite, and quartz (GHCPAPF, 1996). Pyrite appears as euhedral–subhedral grains with variable size, and mainly occurs as banded veins, disseminated grains, and veinlets in the massive quartz or the altered host rocks (Fig. 4A–E). Native gold is locally present along the boundaries or in the fissures of pyrite grains (Fig. 4H). Stibnite is irregular in shape and is present in the quartz veins as isolated grains or as euhedral–anhedral massive aggregates, commonly coexisting with fine quartz and pyrite (Fig. 4C–F).

The later quartz–carbonate stage is marked by the appearance of carbonate and quartz with trace amounts of native gold and pyrite (GHCPAPF, 1996). These minerals fill the fissures in early veins, or occur in the vugs.

4. Samples and analytical methods

4.1. Fluid inclusions

All samples in this study were collected from underground exposures. Fluid inclusions were examined in scheelite and coexisting quartz

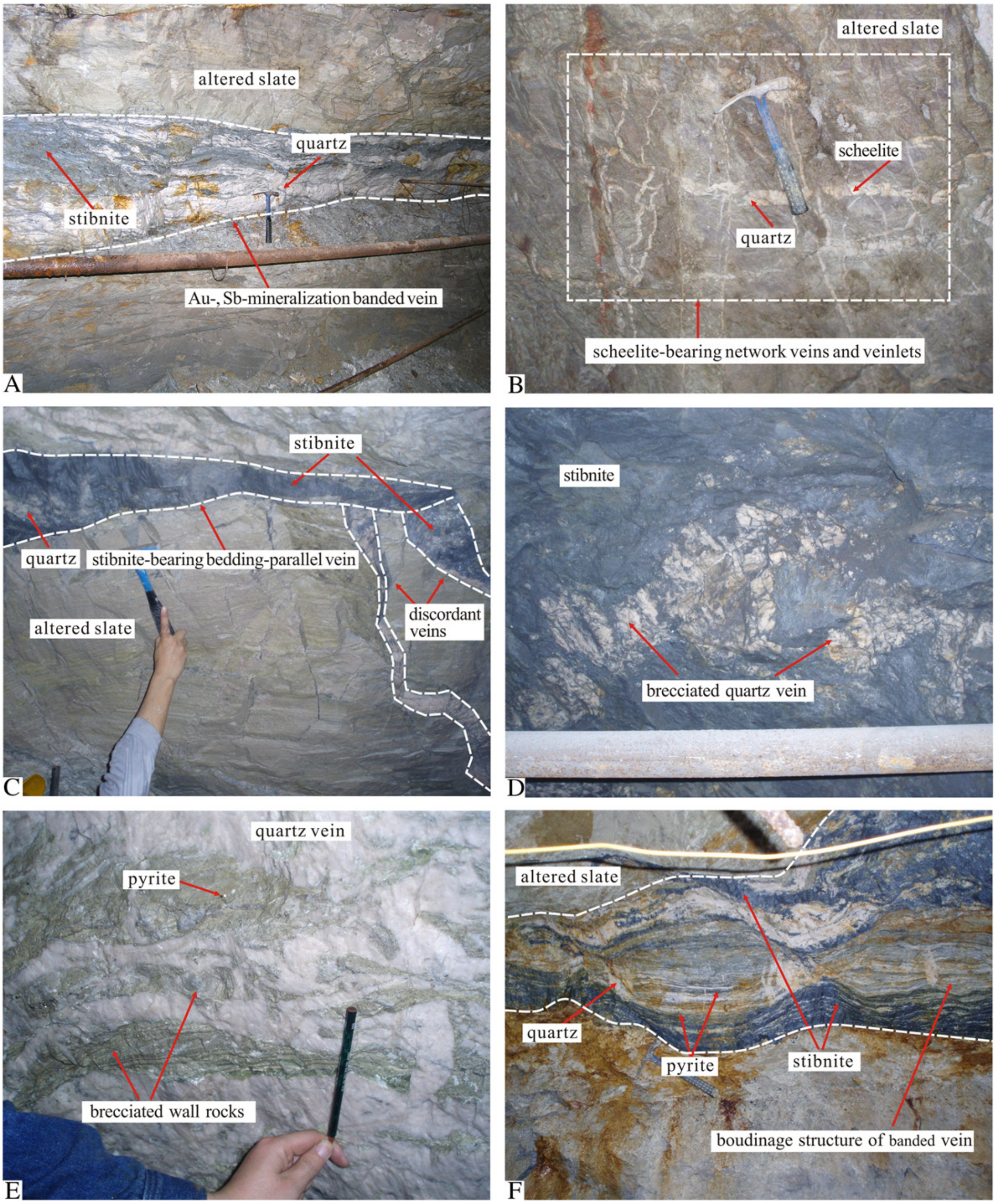
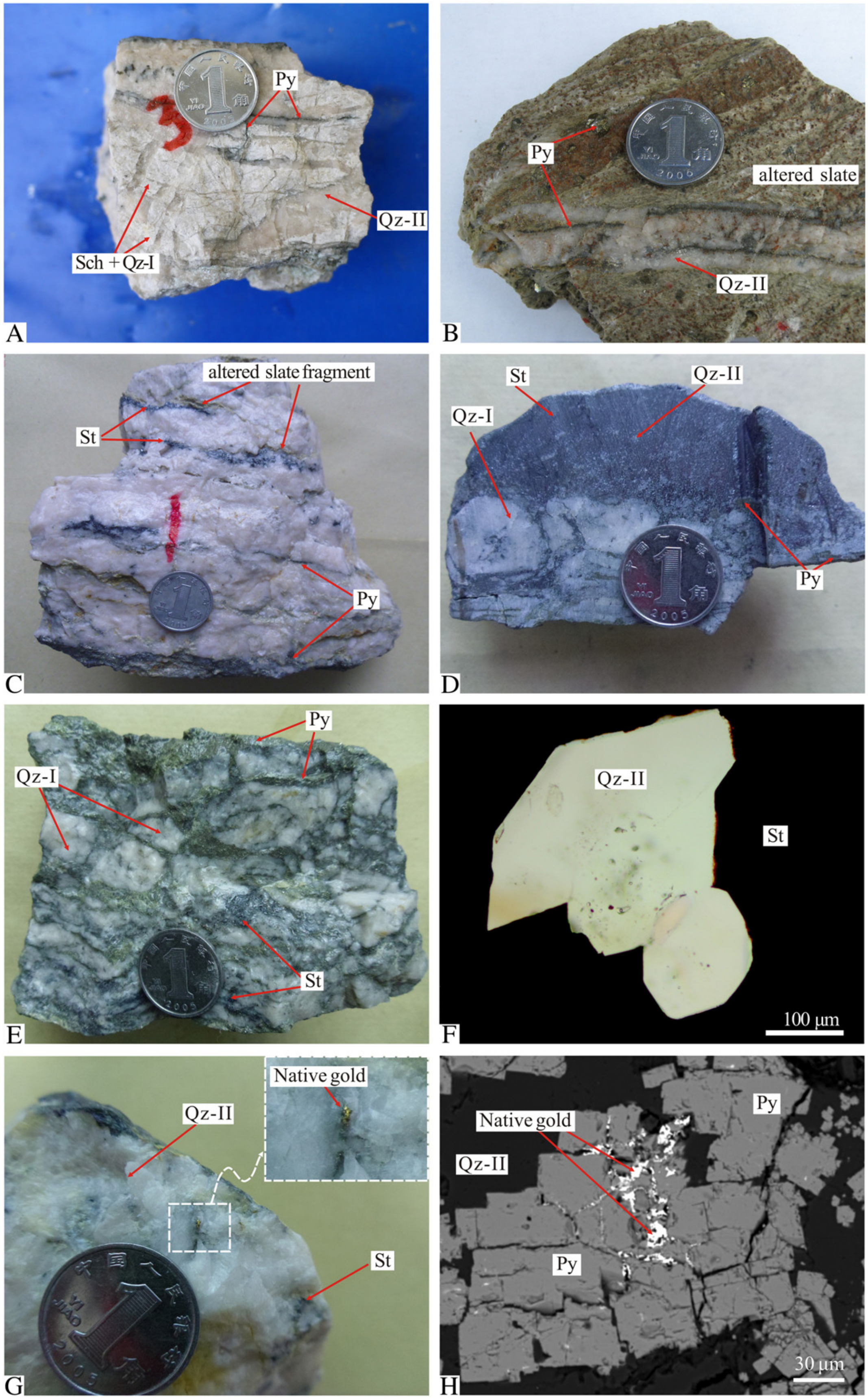


Fig. 3. Occurrences of ore veins in the Woxi deposit. (A) Bedding-parallel banded Au- and Sb-mineralization vein. (B) Quartz–scheelite veinlets intersected at nearly right angles. (C) A pinch-out bedding-parallel vein and two discordant veins. (D) Brecciated quartz vein in massive stibnite. (E) Brecciated host rocks in quartz vein. (F) Boudinage of banded stibnite–gold–quartz vein.

(quartz-I; e.g. Fig. 4A) from the quartz–scheelite veins, and in stibnite and coexisting quartz (quartz-II; e.g. Fig. 4D, F) from the quartz–sulfide–gold veins. Microthermometric measurements of fluid inclusions in stibnite were carried out on a heating–freezing system mounted on an Olympus BH51 infrared microscope. To minimize the effects of the infrared light intensity on the salinity and homogenization temperature of the fluid inclusions in opaque minerals, microthermometric analyses were carried out carefully with the lowest possible light intensity, and with all possible diaphragms nearly closed (Moritz, 2006). Fluid inclusions in scheelite and quartz were measured by a Linkam THMSG 600 programmable heating–freezing stage mounted on a Leica microscope, calibrated with melting-point standards (CCl_4, −22.99 °C; KNO_3,

Fig. 4. Photographs of hand specimen samples and photomicrographs of ore and gangue minerals from the Woxi deposit. (A) Crack-sealing structure. Pyrite and quartz-II filled in the fracture of scheelite-quartz vein. (B) Banded vein. The band is composed of pyrite precipitated during successive hydraulic fracturing events. (C) Banded veins. The bands are composed of pyrite or stibnite or altered slate fragment. (D) Brecciated quartz vein in massive stibnite. (E) Mesh-vein structure. Pyrite and stibnite formed in the mesh fissures of early stage veins. (F) Euhedral fine-grained quartz-II in stibnite. (G) Native gold disseminated in the quartz vein. (H) Native gold occurs along the boundary of pyrite grains. A, D and E reflect the reopening of the early stage veins. Abbreviations for minerals are Py: pyrite; Sch: scheelite; Qz: quartz; St: stibnite.


Py
Qz-II
Sch + Qz-I
A
Py
altered slate
Qz-II
B
altered slate fragment
St
Py
C
St
Qz-II
Qz-I
Py
D
Py
Qz-I
St
E
Qz-II
St
100 μm
F
Native gold
Qz-II
St
G
Py
Native gold
Qz-II
Py
30 μm
H

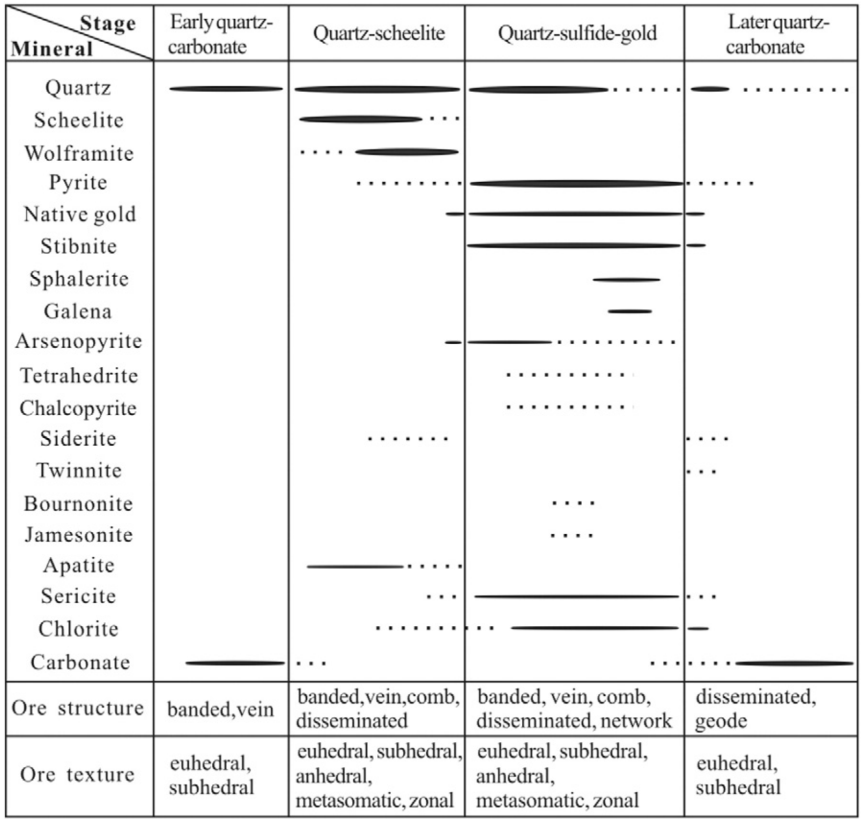


Fig. 5. Paragenetic sequence of minerals from the Woxi deposit (modified after GHCPAPF, 1996).

333 °C) and the melting point of CO_2 (−56.6 °C) in synthetic fluid inclusions. The uncertainty of temperature measurements in this study was approximately ±0.2 °C below 50 °C and ±2 °C above 100 °C. A heating rate of 0.1 °C/min is adopted near the melting temperatures of carbonic phase, clathrate, and ice. Compositions of individual fluid inclusion in quartz and scheelite, including vapour and liquid, were identified by using laser Raman spectroscopy. All of these above experiments were performed at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences.

Salinities of two-phase aqueous inclusions and CO_2-rich inclusions were respectively calculated from the final melting temperature of ice or clathrate following the method proposed by Bodnar (1993) and Lu et al. (2004). Bulk composition and density of aqueous and carbonic phases of the two-phase aqueous inclusions were calculated by using the online calculation (gcmodel.kl-edi.ac.cn/archives/), whereas those of the CO_2-rich inclusions were determined with the MacFlinCor Program (Brown and Lamb, 1989).

4.2. Noble gas isotope

Fresh pyrite and stibnite samples have been collected from the quartz–sulfide–gold veins and their adjacent alteration wall rocks of the Woxi deposit. Noble gas compositions of the fluid inclusions hosted in these samples were released by stepwise heating, which is a powerful and widely adopted technique in noble gas analysis (Bruno et al., 1997; Hou et al., 2011; Kendrick et al., 2001; Rai et al., 2003; Reynolds et al., 1970; Wieler et al., 1986). Pyrite appears to be one of the best preservers for noble gases (Ballentine et al., 2002; Burnard et al., 1999; Hu et al., 1998; Stuart et al., 1994). Due to extremely low concentration of U, Th and K in sulfide, in situ additions of radiogenic ^{4}He and ^{40}Ar in pyrite and stibnite are likely to be negligible. The effect of cosmogenic nuclides can also be ignored because all samples were collected from underground exposures. After these samples were crushed, mineral separates were handpicked under a binocular microscope. The concentrations and isotopic compositions of noble gases were measured using a MM5400 mass spectrometer at the Key Laboratory of Petroleum Resources Research (Lanzhou), Institute of Geology and Geophysics, Chinese Academy of Sciences. The analytical procedures adopted in this study have been described in detail by Ye et al. (2007).

5. Fluid inclusion petrography

Representative samples of scheelite, stibnite, and their corresponding coexisting quartz were selected for fluid inclusion analysis. The quantity and quality of fluid inclusions were relatively variable. The criteria proposed by Roedder (1984) were used to discriminate among primary, pseudosecondary and secondary fluid inclusions. Measurements in this study were only performed on those inclusions considered as primary or pseudosecondary (e.g. Figs. 6–7). These inclusions are mainly classified into four types at room temperature on the basis of phases, phase proportions, and composition: type I (two-phase, liquid-rich aqueous inclusions), type II (type IIa: two-phase CO_2-rich inclusions, and type IIb: three-phase CO_2-rich inclusions), type III (two-phase, vapour-rich aqueous inclusions), and type IV (single-phase aqueous inclusions).

Type I inclusions are the most abundant in all minerals, with the vapour phase ranging from 5% to 45% of the total volume of the inclusions at room temperature. They are negative crystal, elliptical, flat, tubular, or irregular in shape, from a few microns to 20 μm (>50 μm in stibnite) in size, and occur isolated or in groups (Figs. 6A, B, D and E; 7A, B, E, F and H).

Type II inclusions, have not been reported in previous studies (Ding et al., 1981; Dong et al., 2008; Niu and Ma, 1991), but are relatively common in the samples examined in this present study. Large quantities of type II inclusions are observed in scheelite (Fig. 6F) and quartz-II (Fig. 7A, C and D) samples, lesser quantities exist in quartz-I (Fig. 6C), and few are present in stibnite (Fig. 7I). The CO_2 phase of type II inclusions can occupy 15%–90% of the inclusion volumes at room

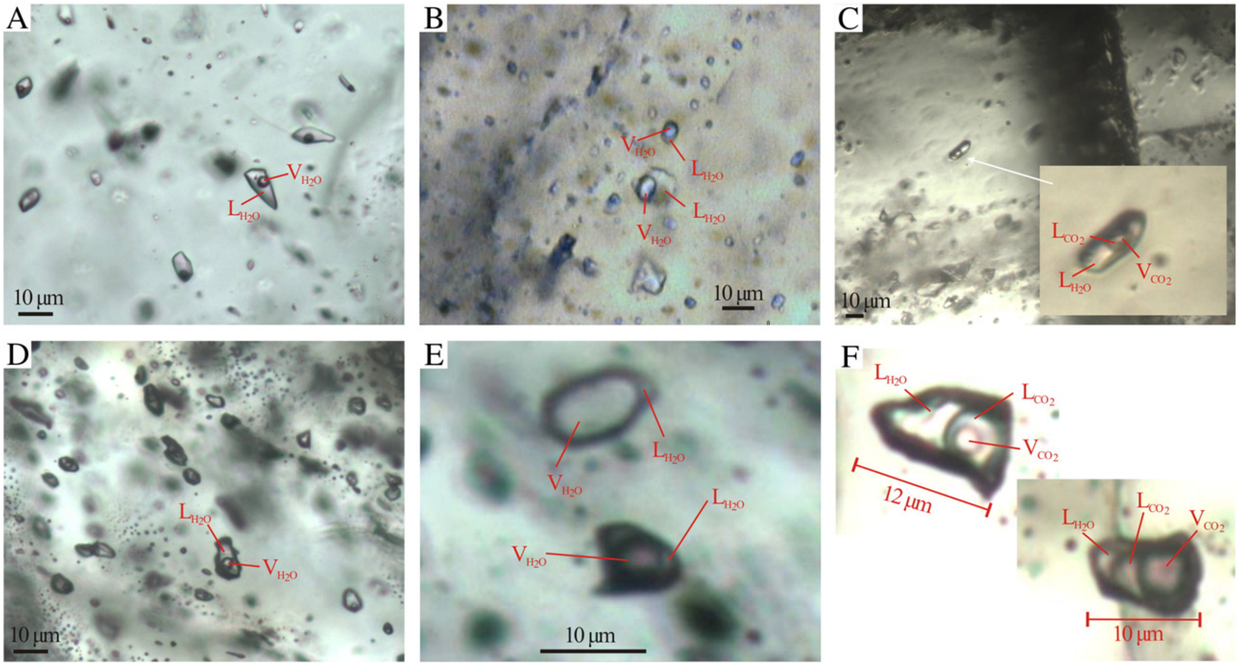


Fig. 6. Photomicrographs of representative fluid inclusion types at room temperature in quartz–scheelite stage. (A) Type I inclusions in quartz-I. (B) Coexistence of type I and type III inclusions in quartz-I. (C) Type II inclusions containing a vapour CO_2 and a liquid CO_2 and H_2O phase in quartz-I. (D) Type I inclusions in scheelite. (E) Coexistence of type I and type III inclusions in scheelite. (F) Type II inclusions in scheelite.

temperature (e.g. Figs. 6F and 7C). These inclusions mainly occur isolated or in groups, with flat or tubular shapes of 4–40 μm in size; type IIb inclusions predominated in the Woxi deposit.

Type III inclusions are scarce in all the selected samples and are characterized by the vapour phase, which constitutes more than 60% of the total volume of the inclusion at room temperature. These inclusions form rounded rectangles and ellipsoids, which are 10–30 μm in diameter, and occur mainly in groups together with type I, type II, and/or type IV inclusions (Figs. 6B, 6E, 7B, 7D and 7G).

Type IV inclusions are rare and mainly found in scheelite and quartz-II samples. They display rounded rectangle shapes, with size varying from a few microns to 10 μm. These inclusions occur in isolation or in groups together with type II inclusions (Fig. 7D).

6. Results

6.1. Microthermometry

Microthermometric studies are mainly carried out on type I and type II inclusions in this study. The cycling method proposed by Goldstein and Reynolds (1994) was adopted for measuring the final melting temperature (T_m) and homogenization temperature (T_h) values in some inclusions whose phase transitions could not be clearly observed. Microthermometric results of fluid inclusions in scheelite and quartz-I from the quartz–scheelite veins as well as stibnite and quartz-II from the later quartz–sulfide–gold veins are summarized in Table 1.

6.1.1. Scheelite

Type I inclusions have eutectic temperatures (T_e) ranging from −27.1 °C to −25.2 °C (Table 1). The final ice-melting temperature ($T_{m\text{-ice}}$) ranges from −3.6 °C to −2.8 °C (n = 14), corresponding to the salinities of 4.65–5.86 wt.% NaCl equiv. (Fig. 8A), with an average of 5.24 wt.% NaCl equiv. Homogenization temperatures (T_h) fall between 151.3 °C and 337.3 °C (n = 78), mostly in the range of 160–240 °C (Fig. 8B). The bulk densities of the ore-forming fluids vary from 0.86 to 0.94 g/cm^3.

Type IIb inclusions form solid CO_2 upon cooling below −95 °C. The final melting temperatures of the solid CO_2 phase ($T_{m\text{-CO2}}$) can reach from −62.7 °C to −56.7 °C (n = 8), indicative of some other volatile components mixed with CO_2, further identified as N_2 by laser Raman spectroscopy. For type IIb inclusions, the CO_2 phase homogenized to liquid ($T_{h\text{-CO2}}$) at the temperatures of 17.7–28.0 °C (n = 18, mean = 24.3 °C), and for type IIa, at 10.3 °C (Fig. 9A). The final clathrate-melting temperatures ($T_{m\text{-clathrate}}$) range from 8.6 °C to 9.1 °C (n = 16), corresponding to salinities of 1.81–2.77 wt.% NaCl equiv. (Fig. 8A). Although some type II inclusions decrepitate before total homogenization, others homogenized to the aqueous phase at the temperatures of 217.0–269.9 °C (n = 11, mostly between 240 °C and 270 °C) and to the CO_2 phase at 286.8 °C. In addition, two type IIa inclusions homogenized to the vapour phase at 258.7 °C and 263.4 °C (Fig. 8B). Their bulk densities range from 0.84 to 0.96 g/cm^3.

6.1.2. Quartz-I

Eutectic temperature of type I inclusion in quartz-I (T_e = −24.5 °C, Table 1) is similar to those measured in scheelite in this study. Type I inclusions have $T_{m\text{-ice}}$ with the range of −3.4 °C to −1.4 °C (n = 7), corresponding to salinities of 2.41–5.56 wt.% NaCl equiv. with a bimodal distribution (Fig. 8C). All type I fluid inclusions homogenized to the liquid phase at temperatures between 162.5 °C and 342.2 °C (n = 34, mostly 200–220 °C; Fig. 8D). The bulk densities of these fluid inclusions vary between 0.89 and 0.92 g/cm^3. Two inclusions of type IIb homogenized to the vapour phase at 258.6 °C and 357.0 °C, with $T_{h\text{-CO2}}$ (homogenized to the CO_2 liquid phase) of 24.3 °C and 26.3 °C, respectively (Fig. 9A). Type III inclusions are rare and only one has been measured in this study, it displays a homogenization temperature (to the vapour phase) of 353.6 °C (Fig. 8D).

6.1.3. Stibnite

$T_{m\text{-ice}}$ of type I inclusions ranges from −3.1 °C to −1.3 °C (n = 39), corresponding to salinities varying from 2.24 to 5.11 wt.% NaCl equiv. (Fig. 10A), with an average of 3.2 wt.% NaCl equiv. Type I inclusions mainly homogenized to the liquid phase within the temperature range of 109.0–273.9 °C (n = 30), with one homogenized to the vapour phase at 190.0 °C, but most in the range of 140–180 °C (Fig. 10B). Two T_h values (248.1 °C and 273.9 °C) of type I inclusions are significantly higher than their actual homogenization temperatures because leaking

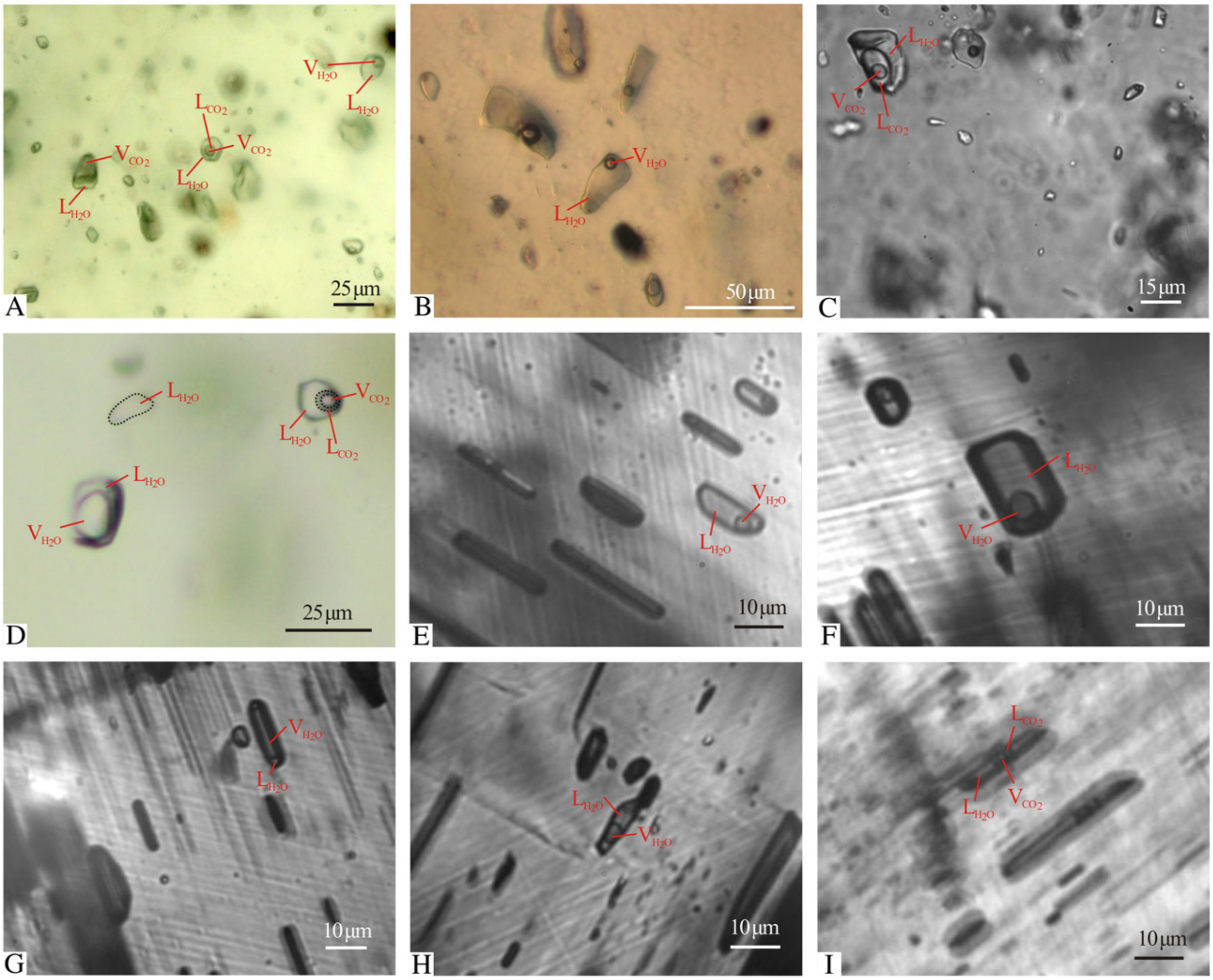


Fig. 7. Photomicrographs of representative fluid inclusion types at room temperature in quartz–sulfide–gold stage. (A) Coexistence of type I and type II inclusions in quartz-II. (B) Coexistence of type I with variable liquid/vapour ratios and type III inclusions in quartz-II. (C) Type II inclusions in quartz-II. (D) Coexistence of type II and type III and type IV inclusions in quartz-II. (E–F) Type I inclusions with tubular shape in stibnite. (G) Type III inclusion in stibnite. (H) Type I inclusion with irregular shape in stibnite. (I) Type II inclusions in stibnite.

probably takes place during heating. Their bulk densities fall in the range of 0.79–0.96 g/cm^3.

6.1.4. Quartz-II

Type I inclusions have T_e with the range of −26.9 °C to −22.3 °C (Table 1). Their $T_{m\text{-ice}}$ values vary from −4.3 °C to −0.5 °C (n = 43), corresponding to the salinities of 0.88–6.88 wt.% NaCl equiv. (Fig. 10C), with an average of 3.47 wt.% NaCl equiv. These fluid inclusions homogenized to the liquid phase within the temperature range of 131.3 °C to 252.4 °C (n = 94), mostly varying between 160 °C and 200 °C (Fig. 10D). The bulk densities vary from 0.83 to 0.98 g/cm^3.

For type IIb inclusions, $T_{m\text{-}CO_2}$ ranges from −57.8 °C to −55.8 °C (n = 16, mean = 56.6 °C). Their $T_{m\text{-clathrate}}$ values fall in between 9.4 °C and 10 °C (n = 17, mean = 9.7 °C), corresponding to the salinities of 0.02–1.22 wt.% NaCl equiv. (Fig. 10C). Some of the type IIb inclusions have $T_{m\text{-clathrate}}$ above 10 °C, always accompanied by $T_{m\text{-}CO_2}$

Table 1
Microthermometric data in the Woxi deposit, western Hunan.

Mineral	Type	Te (°C)	Tm-CO_2 (°C)	Th-CO_2 (°C)	Tm-clathrate or Tm-ice (°C)	Salinity	Th or Th-tot (→L) (°C)	Th or Th-tot (→V) (°C)	D (g/cm^3)
Quartz–scheelite–wolframite stage									
Quartz-I	I	−24.5 (1)			−3.4 to −1.4 (7)	2.41–5.56 (7)	162.5–342.2 (34)		0.89–0.92 (7)
	IIb			24.3–26.3 (2)				258.6–357.0 (2)	
	III						353.6 (1)		
Scheelite	I	−27.1 to −25.2 (2)			−3.6 to −2.8 (14)	4.65–5.86 (14)	151.3–337.3 (78)		0.85–0.94 (11)
	IIa			10.3 (1)				258.7–263.4 (2)	
	IIb		−62.7 to −56.7 (8)	17.7–28.0 (18)	8.6–9.1 (16)	1.81–2.77 (16)	217.0–269.9 (11)	286.8 (1)	0.84–0.96 (9)
Quartz–sulfide–gold stage									
Quartz-II	I	−22.3 to −26.9 (2)			−4.3 to −0.5 (43)	0.88–6.88 (43)	131.3–252.4 (94)		0.83–0.98 (42)
	IIb		−57.8 to −55.8 (16)	17.8–28.0 (26)	9.4–10.0 (17)	0.02–1.22 (17)	189.5–246.2 (16)		0.91–0.96 (13)
Stibnite	I				−3.1 to −1.3 (39)	2.24–5.11 (39)	109.0–273.9 (30)	190.0 (1)	0.79–0.96 (19)

Note: Numbers in parentheses are the number of measurements. Salinity is in wt.% NaCl equiv.

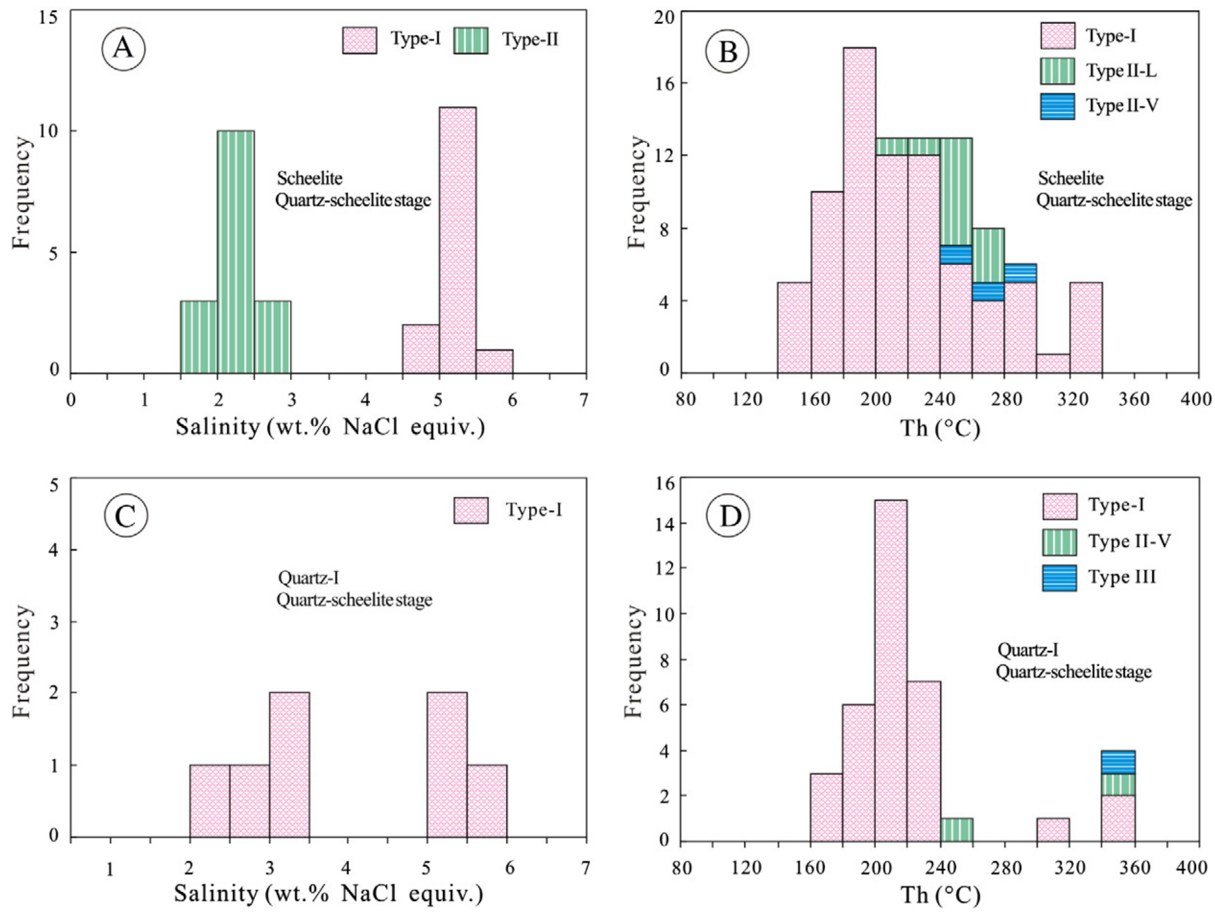


Fig. 8. Histograms of salinities and homogenization temperatures of fluid inclusions in scheelite (A–B) and coexisting quartz-I (C–D) collected from the Woxi deposit.

below −56.6 °C, indicating the presence of volatile components besides CO_2, which have been identified as N_2 by the laser Raman analyses. All the type IIb inclusions homogenized to the aqueous phase within the temperature range of 189.5 °C–357.8 °C (n = 16, mostly varying between 200 °C and 260 °C; Fig. 10D). CO_2 vapour phase homogenized to the liquid phase at temperatures between 17.8 °C and 28.0 °C (n = 26, mean = 23.0 °C) (Fig. 9B). Their corresponding bulk densities vary from 0.91 to 0.96 g/cm^3.

6.2. Raman spectroscopy

A detailed Raman spectroscopic analysis of fluid inclusions in quartz-I and quartz-II was performed. CO_2 is the major non-H_2O volatile component in all fluid inclusions, and minor N_2 was also detected in some fluid inclusions (Fig. 11). The relative higher N_2 concentrations measured in the type II fluid inclusions are consistent with an obvious decrease of the melting point of pure CO_2 in these fluid inclusions.

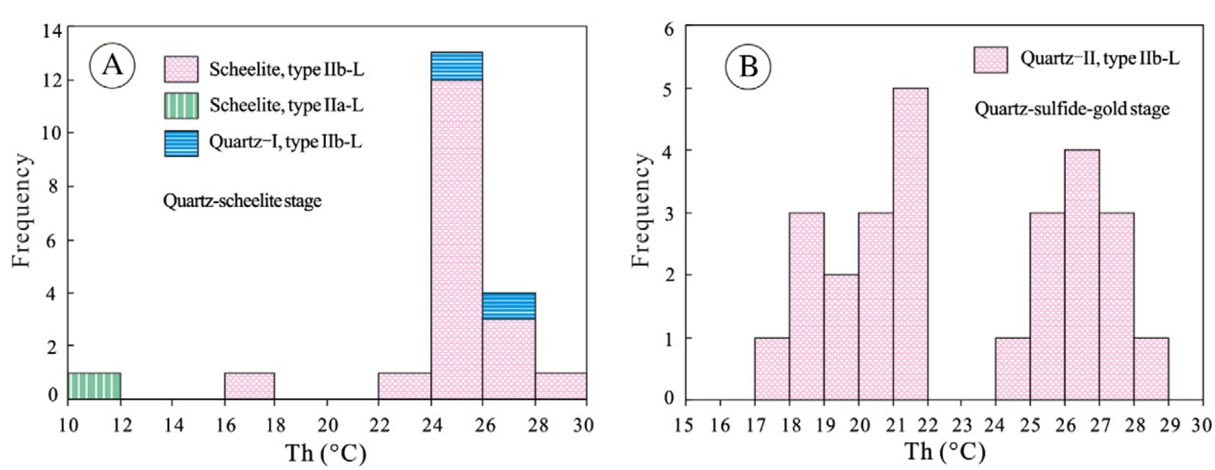


Fig. 9. Histograms of CO_2 homogenization temperatures in scheelite and quartz-I (A) and quartz-II (B) collected from the Woxi deposit.

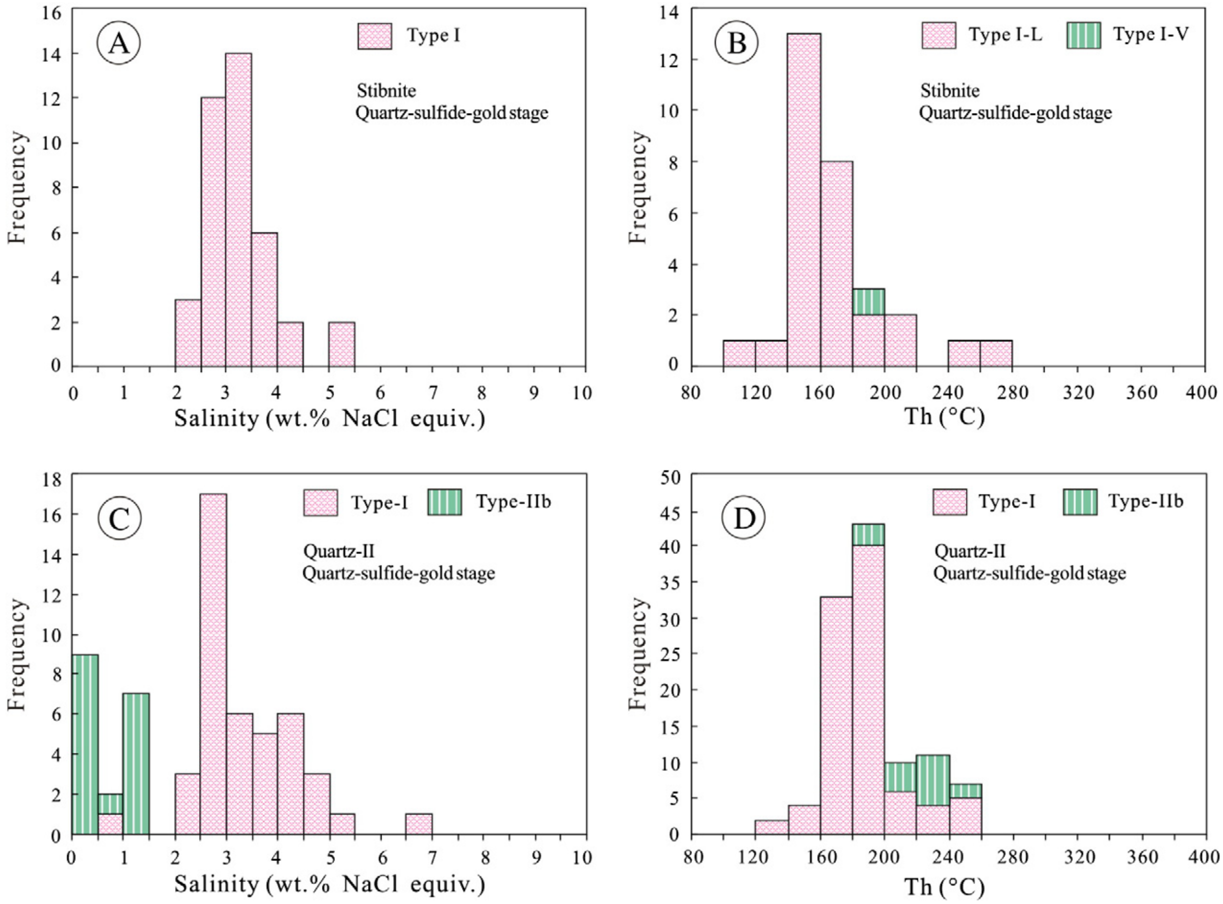


Fig. 10. Histograms of salinities and homogenization temperatures of fluid inclusions in stibnite (A–B) and coexisting quartz-II (C–D) collected from the Woxi deposit.

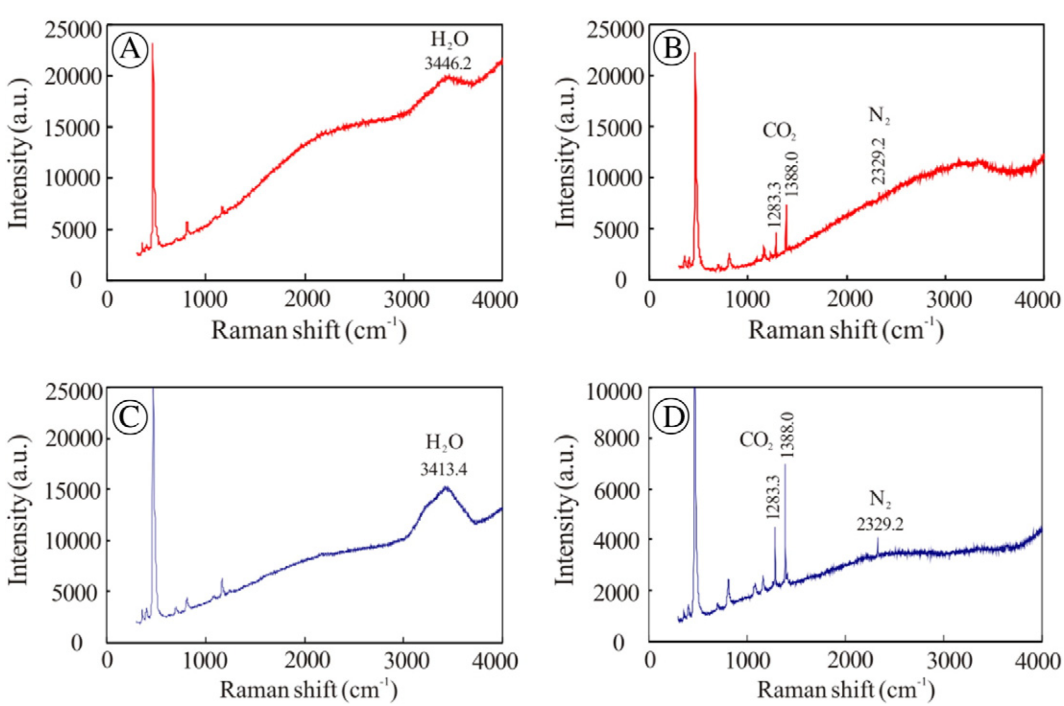


Fig. 11. Representative Raman spectra of fluid inclusions in quartz-I (A–B) of quartz–scheelite stage and quartz-II (C–D) of quartz–sulfide–gold stage. A and C show that the vapour bubbles are mainly of H_2O; B and D show that the bubbles contain some N_2 in addition to CO_2.

Table 2
Noble gas compositions and isotopic ratios of fluid inclusions trapped in pyrite and stibnite samples from the Woxi deposit, western Hunan.

Sample	Mineral	^3He (E^{-12})	^4He (cm^3STP/g) (E^{-7})	^{40}Ar (cm^3STP/g) (E^{-7})	^{36}Ar (cm^3STP/g) (E^{-7})	$^3He/^4He$ (Ra)	$^{40}Ar/^{36}Ar$	$^4He/^{36}Ar$	$\%^{40}Ar_E$	F^4He
WX-119	Pyrite	0.021	428	10.22	0.008	0.005	1341.7	56,189	78	339,508
WX-155	Pyrite	0.009	417	4.41	0.007	0.002	624.2	59,023	53	356,634
XXJK-34	Pyrite	0.017	396	1.97	0.001	0.004	2585.9	519,805	89	3,140,817
WX-159	Pyrite	0.025	486	2.05	0.003	0.005	722.2	171,214	59	1,034,527
XXJK-33	Pyrite	0.047	551	11.34	0.008	0.009	1446.1	70,265	80	424,560
XXJK-35	Pyrite	0.097	512	2.63	0.004	0.019	698.1	135,904	58	821,171
WX-121	Pyrite	0.030	166	5.00	0.003	0.018	1715.9	56,968	83	344,217
WX-146	Pyrite	0.038	522	5.92	0.011	0.007	528.8	46,659	44	281,926
WX-27-3	Pyrite	0.486	294	2.49	0.009	0.165	281.3	33,240	–	200,849
WX-24-5	Pyrite	0.112	80	1.15	0.005	0.139	247.0	17,176	–	103,785
WX-27-1	Pyrite	0.304	356	2.93	0.008	0.086	388.6	47,269	24	285,615
WX-23-12	Pyrite	0.111	139	1.80	0.007	0.080	264.2	20,445	–	123,537
XXJK-21	Pyrite	0.036	156	5.15	0.022	0.023	229.9	6990	–	42,235
WX-23-10	Stibnite	0.005	7	9.39	0.027	0.063	347.8	275	15	1663
WX-28-5	Stibnite	0.366	130	15.24	0.036	0.281	420.0	3591	30	21,698
WX-34-4	Stibnite	0.004	17	13.29	0.051	0.022	260.3	328	–	1983
YRS-15	Stibnite	0.005	11	7.53	0.024	0.044	313.6	470	6	2843
WX-24-8	Stibnite	0.016	62	20.82	0.042	0.026	495.0	1471	40	8887
XXJK-15	Stibnite	0.014	50	7.01	0.015	0.028	468.4	3310	37	20,000

Note: F^4He values reflect enrichment of ^4He in the fluid relative to air; $F^4He = (^4He / ^{36}Ar)_{sample} / (^4He / ^{36}Ar)_{air}$ where $(^4He / ^{36}Ar)_{air} = 0.1655$ (Kendrick et al., 2001).

6.3. Noble gas isotopes

Pyrite and stibnite samples analysed in this study are well-crystallized euhedral grains without any obvious subsequent deformation. With the exception of eight pyrite samples collected from the altered wall rocks, all the remaining samples show a paragenesis with quartz-II in the quartz–sulfide–gold veins. Therefore, we are confident that the extracted fluids from those sulfides (especially from the veins) are related to hydrothermal mineralization, and thus they should be identical to the fluid inclusions hosted in the quartz-II and stibnite in this study. Because in-situ additions of radiogenic ^4He and ^{40}Ar and cosmogenic nuclides are negligible for these sulfide samples collected from underground exposures, the measured compositions of noble gas isotopes can truly represent the initial composition of the fluid inclusions.

The noble gas isotope compositions of fluid inclusions in the samples mentioned above are listed in Table 2. The data show that ^4He concentrations vary from 7 to 551×10^{-7} cm^3STP/g and ^{40}Ar concentrations fall in between 1.15 and 20.82×10^{-7} cm^3STP/g. The $^3He/^4He$ ratios vary in the range of 0.002–0.281 Ra (Ra $= 1.4 \times 10^{-6}$ for air). The $^{40}Ar/^{36}Ar$ ratios vary from 229.9 to 2585.9. The F^4He values for the hydrothermal fluids at Woxi, defined as $F^4He = (^4He / ^{36}Ar)_{sample} / (^4He / ^{36}Ar)_{air}$ where $(^4He / ^{36}Ar)_{air} = 0.1655$ (Kendrick et al., 2001), are above 1000 (Table 2).

7. Discussion

7.1. Nature of ore-forming fluids

At the quartz–scheelite stage, fluid inclusions trapped in scheelite and quartz-I display the same types (Fig. 6) and largely share similar temperatures and salinities (Fig. 8). The majority of fluid inclusions in scheelite and quartz-I have homogenization temperatures in the range of 180–240 °C and 200–220 °C, respectively. The salinities of fluid inclusions in quartz-I and scheelite exhibit a bimodal distribution (Fig. 8A and C). Some fall in between 1.5 and 3.5 wt.% NaCl equiv. with a mode around 2.0 wt.% NaCl equiv., while the others vary between 4.5 and 6.0 wt.% NaCl equiv. with a mode at 5.0 wt.% NaCl equiv. The lower salinities in scheelite were determined from the final clathrate-melting temperatures of type II inclusions, and those relatively higher salinities were determined from the final ice-melting temperatures of type I inclusions. However, all the lower and higher salinity inclusions in quartz-I were determined from the final ice-melting temperatures of type I inclusions. An alternative explanation for the low salinities for type I inclusions in quartz-I is that these inclusions also contain minor heterogeneously-trapped CO_2 (but undetected by the conventional petrography observations and microthermometric measurement) (Guillemette and Williams-Jones, 1993). Such heterogeneous entrapment of CO_2 will result in anomalously high homogenization temperatures (Guillemette and Williams-Jones, 1993), which is consistent with the higher homogenization temperatures of the quartz-I hosted type I inclusions determined in this study (Fig. 8D). Therefore, it can be concluded that the fluid inclusions in scheelite and quartz-I probably have been trapped under a similar condition during the tungsten mineralization, consistent with the intergrown texture of scheelite and quartz-I in these samples.

At the quartz–sulfide–gold stage, most inclusions in stibnite are type I, whereas quartz-II hosts a range of inclusion types (except type IV) (Fig. 7A–I). Fluid inclusions in stibnite and quartz-II display similar microthermometric results (Fig. 10). Homogenization temperatures of fluid inclusions in stibnite mostly vary from 140 to 180 °C (Fig. 10B), and those in quartz-II fall in between 160 and 200 °C (Fig. 10D). Salinities of fluid inclusions in stibnite and quartz-II are mostly in the range of 2.5–4.0 wt.% NaCl equiv. and 2.5–4.5 wt.% NaCl equiv., respectively (Fig. 10A, C). This is consistent with the fact that stibnite commonly coexists with quartz-II (Fig. 4F).

According to many previous studies (e.g. Bailly et al., 2000; Campbell and Panter, 1990; Wang et al., 2013; Wei et al., 2012), the homogenization temperatures and salinities of fluid inclusions in ore minerals are distinct from those in coexisting gangue minerals. However, the consistency of fluid inclusions in ore minerals and gangue minerals also have been previously reported (e.g. Kucha and Raith, 2009). In this study, fluid inclusions in ore minerals (scheelite and stibnite) and their corresponding coexisting quartz share similar characteristics. The ore-forming fluids of the Woxi deposit are characterized by low-to-moderate temperatures, low salinities, CO_2-rich and N_2-bearing aqueous fluids. Likewise, fluid inclusions from other lode gold deposits in the Xuefengshan Range mainly include H_2O-rich aqueous inclusions and CO_2-rich inclusions with large variable liquid/vapour ratios. Their homogenization temperatures range from 100 °C to 330 °C (mostly 150–200 °C) and their salinity values are lower than 9 wt.% NaCl equiv. (Chen and Yu, 1994; Ding and Wang, 2009; He et al., 1996; Lu et al., 2012; Niu and Ma, 1991; Yao and Zhu, 1993; Yu, 1997). Minor components of N_2 and/or CH_4 are also detected in the vapour phase by laser Raman spectroscopy (Lu et al., 2012).

7.2. Sources of ore-forming fluids

The ore-forming fluids characterized by CO_2-rich may be derived from magmatic water (Fan et al., 2003; Yang et al., 2012, 2013), metamorphic water (Fairmaid et al., 2011; Goldfarb et al., 1988; Harlov, 2012; Lamadrid et al., 2013; Lawrence et al., 2013) or mantle (Luque et al., 2014; Mao et al., 2003; Tripathi et al., 2012; Xu et al., 2013). Although previous studies reveal that the $\delta^{18}O$ values of mineralization fluids in the Woxi deposit vary between 2.0‰ and 13.6‰ (Chen, 2012; Luo et al., 1984), these oxygen data cannot discriminate between a metamorphic or magmatic or evolved meteoric source.

The noble gas data determined in this study allow us to further evaluate these possible sources for the ore-forming hydrothermal fluids. Compared with the higher concentrations of ^4He in coexisting pyrite from veins ($80–356 \times 10^{-7}$ cm^3 STP/g), the lower values in intergrown stibnite ($7–130 \times 10^{-7}$ cm^3 STP/g) can be best explained by He loss (e.g. Hu et al., 1999b), since the helium diffusion is extremely slow in pyrite (Baptiste and Fouquet, 1996). However, the $^3He/^4He$ ratios for stibnite (mean of 0.099 Ra) are similar to those for coexisting pyrite (mean of 0.077 Ra), indicating that the mass fractionation of He caused by He loss in stibnite could be negligible (Fig. 12). The extremely low concentrations of ^3He ($0.009–0.486 \times 10^{-12}$ cm^3 STP/g) in pyrite and helium isotope ratios (0.002–0.281 Ra) in all pyrite and stibnite provide reliable evidence that He can't be originated from a mantle source ($>3 \times 10^{-12}$ cm^3 STP/g, Burnard et al., 1999; or 7–9 Ra, Ozima and Podosek, 2002).

Because even small magmatic additions to crustal fluid systems are readily detected (Ballentine et al., 2002), the involvement of magmatic fluids in many hydrothermal deposits are characterized by $^3He/^4He$ ratios commonly more than 0.1 Ra (e.g. Burnard et al., 1999; Sun et al., 2009; Zhu et al., 2013). In South China, the maximum $^3He/^4He$ ratios for many intrusion-associated gold, tungsten, and tin deposits are above 1 Ra (Burnard et al., 1999; Cai et al., 2012; Hu et al., 1997, 1999a, 2004; Sun et al., 2006; Zhai et al., 2012). Nevertheless, in the Woxi deposit, with the exception of sample WX-27-3 (0.165 Ra), WX-24-5 (0.139 Ra) and WX-28-5 (0.281 Ra), all the helium isotope ratios in the remaining samples are less than 0.1 Ra (Table 2). This probably indicates that the ore-forming fluids responsible for gold, antimony, and tungsten mineralization in Woxi are not of magmatic in origin. Moreover, as the F^4He values for sulfides in this study (>1000, Table 2) are remarkably higher than that for the atmosphere ($F^4He = 1$, Kendrick et al., 2001) and ASW ($F^4He = 0.18–0.28$, Kendrick et al., 2001), the fluids in Woxi probably contain negligible contributions from atmospheric He, the measured $^3He/^4He$ ratios are probably derived from a crustal He source.

The estimated $^{40}Ar/^{36}Ar$ ratios range from 229.9 to 2585.9 (Table 2). $^{40}Ar/^{36}Ar$ values lower than the atmospheric ratio of 295.5 have mainly been interpreted to be the result of mass fractionation (Nagao et al., 1979, 1981; Schaaf and MÜller-Sohnius, 2002; Singer and Brown, 2002) and perhaps require a non-geological explanation (Singer and Brown, 2002), while those higher than 295.5 indicate a significant proportion of excess ^{40}Ar ($^{40}Ar_E$) from a mantle or crustal origin. Because a minor addition of mantle component will dramatically change the He isotopic composition, the $^{40}Ar_E$ (up to 89%, Table 2) is probably derived from a crustal source rather than a mantle component, and might be generated by the host rocks or old basement (Fairmaid et al., 2011; Kendrick et al., 2002). This is consistent with the extremely high Sr isotope compositions in scheelite (0.743–0.750; Peng et al., 2003b; Peng and Frei, 2004) and in fluid inclusions in quartz coexisting with stibnite (0.754–0.766; Shi et al., 1993) in this deposit, which has been considered to be a result of either preferential leaching of Proterozoic rocks or leaching of the underlying older rocks (Peng et al., 2003b).

7.3. Mineralization mechanism

Mixing and boiling are the most important physical processes affecting ore deposition (Wilkinson, 2001). Fluid mixing has been recognized in many tungsten deposits worldwide (e.g. Beuchat et al., 2004; Wei et al., 2012; Yokart et al., 2003). Noticeably, boiling is an efficient mechanism for gold precipitation in many lode gold deposits (e.g. Sigma deposit, Canada, Robert and Kelly, 1987; Bronzewing deposit, Australia, Dugdale and Hagemann, 2001; Wiluna deposits, Australia, Hagemann and Lüders, 2003; Wangfeng deposit, China, Zhang et al., 2012), and some stibnite deposits (Bailly et al., 2000; Guillemette and Williams-Jones, 1993).

In the Woxi deposit, during the early quartz–scheelite stage, the fluids contain variable amounts of N_2 suggesting that the mineralizing solutions reacted either directly with the host rocks or with fluids trapped within the host rocks (Mernagh, 2001; Polito et al., 2001). Peng et al. (2005) also proposed that aqueous effects or water–rock interaction is responsible for scheelite precipitation in Woxi based on the REE tetrad-effect characteristics in scheelite. Moreover, a positive relationship between homogenization temperatures and salinities of most aqueous inclusions in scheelite and quartz-I as shown in Fig. 13, further reveals that a hotter, saline fluid mixed with a cooler, dilute fluid (Wilkinson, 2001). Therefore, fluid mixing between deep crustal fluid and host-rock-buffered fluid is a possible mechanism associated with scheelite precipitation in the Woxi deposit.

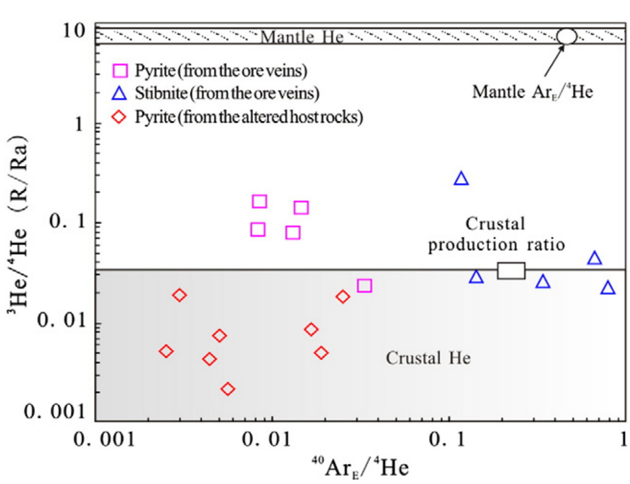


Fig. 12. $^3He/^4He$ vs. $^{40}Ar_E/^4He$ diagram for fluid inclusions in pyrite and stibnite collected from the Woxi deposit.

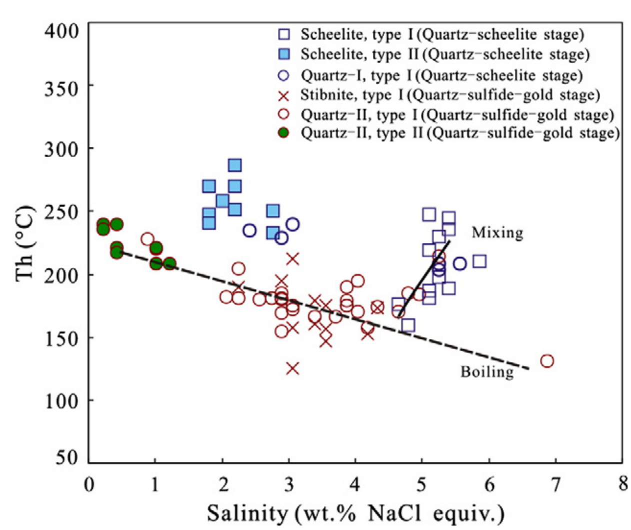


Fig. 13. Homogenization temperature vs. salinity of different types of fluid inclusions at the quartz–scheelite stage and quartz–sulfide–gold stage.

In contrast, fluid inclusion petrography and microthermometric data for the quartz–sulfide–gold stage provide evidence for boiling. Three types of fluid-inclusion assemblages are observed: (1) type I, IIa, and IIb inclusions (Fig. 7A); (2) type I aqueous inclusions with considerable variable liquid/vapour ratios and type III inclusions (Fig. 7B); (3) type IIb, III, and IV inclusions (Fig. 7D). All fluid-inclusion assemblages usually display roughly similar homogenization temperature, indicative of fluid boiling (Ramboz et al., 1982; Van den Kerkhof and Hein, 2001; Wilkinson, 2001). A negative correlation between the homogenization temperature and salinity for most inclusions (Fig. 13), and the common occurrence of H_2O-rich, higher salinity inclusions coexisting with CO_2-rich, lower salinity type II inclusions in this study can also be best explained by fluid boiling (Chen et al., 2012b; Fan et al., 2009; Liu et al., 2013; Mernagh, 2001; Pichavant et al., 1982; Wilkinson, 2001). Previous studies suggest that H_2S prefers to enter the vapour phase during boiling, and sulfur decrease in the fluids probably results in gold deposition (Guillemette and Williams-Jones, 1993; Naden and Shepherd, 1989). Thus, it can be concluded that boiling is critical for gold and stibnite deposition in the Woxi deposit.

Moreover, boiling is probably caused by an abrupt drop in pressure (Wilkinson, 2001) induced by the fault-valve mechanism (McCuaig and Kerrich, 1998; Sibson et al., 1988) in hydrothermal systems, because structural evidences for fluid-pressure fluctuations shown in Figs. 3D–F and 4A–E are common in the Woxi mining district. In order to evaluate the fluid-pressure conditions at the time of entrapment, the isochores of type I inclusions were estimated by the online calculation (gcmodel.kl-edi.ac.cn/archives/); the isochores of type II inclusions were calculated with the equation of state for NaCl–H_2O–CO_2 proposed by Brown and Lamb (1989). At 182 °C, which is the average homogenization temperature of type I fluid inclusions at the quartz-sulfide-gold stage, the pressure is estimated to be between 960 and 1850 bars.

7.4. Orogenic-type model for the Woxi Au–Sb–W deposit

Several genetic models have been proposed for this deposit, including (1) a sedimentary exhalative (SEDEX) origin (Gu et al., 2007, 2012; Zhang, 1985), (2) a magmatic-hydrothermal origin (Mao and Li, 1997; Peng and Frei, 2004), and (3) a metamorphic-hydrothermal origin (Luo et al., 1984; Yang, 1992). However, the low salinity, CO_2-rich and N_2-bearing aqueous fluid associated with Au–Sb–W mineralization at Woxi is significantly different from the SEDEX type deposits, the latter usually have higher salinity (3.5–15 wt.% NaCl equiv.) without CO_2-rich fluid inclusions (Canet et al., 2003; Chen et al., 2007; Lott et al., 1999). The marked radiogenic ^{87}Sr-rich ore-forming fluids (0.743–0.750; Peng et al., 2003b; Peng and Frei, 2004) for the Woxi deposit is not compatible with a SEDEX origin (Peng et al., 2003b). Whereas, the relatively low temperature and salinity values for the Woxi deposit are different to those typical for magmatic-hydrothermal deposits.

Instead, the geological and geochemical features documented in Woxi are compatible with orogenic gold deposits (Goldfarb et al., 2005; Groves et al., 1998; Groves et al., 2003; Kerrich et al., 2000; McCuaig and Kerrich, 1998; Ridley and Diamond, 2000). The Woxi deposit occurs in an intracontinental orogenic setting of the Xuefengshan Range (Chu et al., 2012; Li et al., 2009; Zhang et al., 2013). Orebodies are predominantly quartz veins with minor pyrite, which are hosted by shear zones in metamorphosed turbidites. Moreover, the low-to-moderate temperature, low-salinity, H_2O–CO_2–NaCl deeply-derived crustal fluid with $\delta^{18}O$ and δD values (2.0–13.6‰, −81 to −64‰; Luo et al., 1984; Chen, 2012) at Woxi is consistent with many orogenic gold fluid studies worldwide (e.g. Goldfarb et al., 2001; Groves et al., 1998; Kerrich et al., 2000). However, compared to gold-only orogenic deposits, the Woxi deposit exhibits the atypical element association of Au–Sb–W, thus setting it apart from most orogenic gold deposits.

8. Conclusions

(1) In the Woxi Au–Sb–W deposit, the fluid inclusions in ore minerals and corresponding intergrown quartz largely share similar characteristics, and yield homogenization temperatures of 180–240 °C in the quartz–scheelite veins, and 140–200 °C in later quartz–sulfide–gold veins.
(2) The ore-forming fluids in Woxi are characterized by low salinity, low-to-moderate temperature, CO_2-rich and N_2-bearing aqueous fluids, consistent with other lode gold deposits in the Xuefengshan Range. They are dominated by deeply non-magmatic crustal origin fluids, with a minor contribution of meteoric water or wallrock-buffered fluid.
(3) Fluid mixing is a possible mechanism for early scheelite precipitation, but boiling caused by the marked pressure drop is critical to gold and stibnite deposition in the Woxi deposit.
(4) The Woxi Au–Sb–W deposit is probably an atypical orogenic gold deposit with significant tungsten and antimony mineralization.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Grants No. 40673021, 41073036, 41272096) and the National Special Research Programs for Non-Profit Trades (Sponsored by MLR, Grant No. 200911007). The authors give special thanks to the geologists and miners of the Woxi mining district, for their enthusiastic help during the field investigation. Prof. Su Wen-Chao is thanked for his warm-hearted help during data processing. Prof. Lu Huan-Zhang is acknowledged for his comments on the microthermometric results. Our thanks are also due to an anonymous reviewer for the careful and constructive comments and suggestions, which significantly improved the manuscript. Lastly, critical reviews by Prof. Franco Pirajno are greatly appreciated.

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