Geochronology and Ore Genesis of the Niujuan-Yingfang Pb-Zn-Ag Deposit in Fengning, Northern North China Craton: Constraints from Fluid Inclusions, H-O-S Isotopes and Fluorite Sr-Nd Isotopes

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ABSTRACT: The Niujuan-Yingfang Pb-Zn-Ag deposit in northern North China Craton (NCC) is hosted at the contact zone between Permian biotite monzogranite and Hongqiyiyingzi Group migmatitic gneiss. The orebodies are structurally controlled by NE-trending F3 fault. Mineralization can be divided into three stages: (1) siliceous-chlorite-pyrite stage, (2) quartz-Ag-base metal stage, and (3) fluorite-calcite stage. Four types of fluid inclusions were identified, including: (1) liquid-rich aqueous inclusions, (2) vapor-rich inclusions, (3) liquid-rich, solid-bearing inclusions, and (4) CO2-bearing inclusions. Microthermometric measurements reveal that from stage I to III, the homogenization temperatures range from 317 to 262 °C, from 297 to 192 °C, and from 248 to 151 °C, respectively, and the fluid salinities are in the ranges from 1.1 wt.% to 6.5 wt.%, 1.2 wt.% to 6.0 wt.% and 0.7 wt.% to 4.0 wt.% NaCl equivalents, respectively. Fluid boiling and cooling are the two important mechanisms for ore precipitation according to microthermometric data, and fluid-rock interaction is also indispensable. Laser Raman spectroscopic analyses indicate the fluid system of the deposit is composed of CO2-NaCl-H2O-S-N2. Metallogenic fluorites yielded a Sm-Nd isochron age of 158±35 Ma. The δ34S values of sulfides range from -1.3‰ to 6.3‰, suggesting that the sulfur may be inherited from the basement metamorphic igneous rocks. Hydrogen and oxygen isotopic compositions of quartz indicate a metamorphic origin for the ore-forming fluid, and the proportion of meteoric water increased during the ore-forming processes. Sr-Nd isotopes of fluorites show a crustal source for the ore-forming fluid, with primary metamorphic fluid mixed with meteoric water during ascent to lower crustal levels. Combined with the geological, metallogenic epoch, fluid inclusions, H-O-S and Sr-Nd isotopes characteristics of the deposit, we suggest that the Niujuan-Yingfang deposit belongs to the medium-low temperature hydrothermal vein-type Pb-Zn-Ag polymetallic deposit with ore-forming fluids dominantly originated from metamorphic fluids.

KEY WORDS: fluid inclusion, geochronology, H-O-S isotopes, fluorite Sr-Nd isotopes, Niujuan-Yingfang Pb-Zn-Ag deposit, NCC.

0 INTRODUCTION

The middle segment of the northern margin of the North China Craton (NCC) is one of the important Ag-polymetallic ore deposit belts in China. There are more than 80 deposits in this area, such as the Caijiaying Pb-Zn-Ag deposit (Huang et al., 1997), Xiangguang Mn-Ag deposit (Liu et al., 2012), Xiaokouhuaying Mn-Ag deposit (Guo and Wang, 1998), Guzigou Pb-Zn-Ag deposit (Wang, 2015), Beichagoumen Pb-Zn-Ag deposit (Mao et al., 2000), Wanquansi Ag-Au deposit (Liu Q M et al., 2018) and Niujuan-Yingfang Pb-Zn-Ag deposit etc. (Fig. 1). Three metallogenic belts and one ore-concentrated district can be identified, including the NE-trending Lingqiu-Ongniu Banner metallogenic belt, the EW-trending Chicheng-Fengning-Longhua-Yantongshan metallogenic belt, the EW-trending Miyun-Xinglong-Xiefengkou-Jingzhou-Yixian metallogenic belt, and the ore-concentrated district among the Zhangbei-Guyuan-Kangbao area in the northwest of Hebei Province (Mao et al., 2002). The Lingqiu-Ongniu Banner metallogenic belt, located in the Xuefeng Mountain-Taihang Mountain-Great Hinggan Range NE-trending tectonic belt, is situated between two deep faults called the Datong-Zhangbei-Zhenglan Banner and Zijinguan-Changping-Ongniu Banner, and the Ag-polymetallic mineralization is controlled by the...
Shanghuangqi-Wulonggou Mesozoic tectono-magmatic complex belt and its secondary fault magmatic belt (Fig. 1). Such belt contains 70% of the Ag-polymetallic deposits in this area, including the Niujuan-Yingfang Pb-Zn-Ag deposit of this paper. Extensive studies have been done on these typical Ag-polymetallic deposits in terms of the geological, geochemical, metallogenic chronology, ore-forming fluid and ore genesis (Liu et al., 2017; Zhang, 2014; Li et al., 2016, 2014; Mao D B et al., 2005, 2002, 2000; Gao, 2004; Yang M Z, 2000; Guo and Wang, 1998; Huang et al., 1997). There are four types of Ag-polymetallic deposits (Mao et al., 2002), including: (1) sedimentary exhalation type (e.g., the Gaobanhe deposit), (2) superimposed type (e.g., the Bajiazi deposit), (3) epithermal type associated with alkaline volcanic activity in the Dahongyu Period (e.g., the Dongzigou deposit), and (4) magmatic hydrothermal type associated with volcanic-porphyry activity in the Mesozoic (e.g., the Xiangguang, Beichagoumen and Niujuan-Yingfang deposit; Gao, 2017; Li et al., 2017; Wang, 2010; Xu, 1991). The mineralization is characterized by multi-period and multi-genesis, with the Yanshanian Period (195–100 Ma) as the most important metallogenic period. These Ag-polymetallic deposits are mainly controlled by continental volcanic-subvolcanic rocks and volcanic-faulted basins in the Mesozoic with magmatic hydrothermal origin, and most of them are distributed in the transition zone between continental volcanic-sedimentary basin and magmatic belt. However, the ore-forming age and ore genesis is still disputable for each deposit. For example, as the largest vein-type Pb-Zn-Ag deposit in China, the Caijiaying deposit was shown to have formed in the Mesozoic with zircon U-Pb age of 119.1 Ma from the genetic-related quartz porphyry vein (Mao et al., 2003). However, geological data suggest that the mineralization underwent multiple stages of evolution, including early submarine sedimentary mineralization, and late-stage transformation and re-mobilization of the source deposits associated with the Mesozoic magmatism (Mao et al., 2002). Thus, it is of great significance to further study the typical deposits, which aims to better understand the regional metallogenic processes.

The Niujuan-Yingfang Pb-Zn-Ag deposit, discovered in the 1990s by No. 514 Geological Team, North China Bureau of Nonferrous Geological Exploration, is one of the important Ag-polymetallic deposits in the northern Hebei (Li Y J et al., 2017; Li J M et al., 2006a; Nie et al., 2007; Yang S D, 2000). The deposit has an estimated silver reserve of 652 tons with average grade of 277.85 g/t and subordinate combined Pb-Zn reserves of about 200,000 tons (Wang et al., 2018). Many studies have been carried out since the discovery of this deposit, including studies on ore deposit geology (Wang et al., 2018; Wang and Liu, 2009; Li et al., 2007, Li et al., 2006a; Li and Wang, 2002; Fu and Gao, 1998; Ren, 1991), geochronology (Li Y J et al., 2017; Li Z Y et al., 2014; Nie et al., 2007; Liu and Zhang, 1996), ore-forming fluid characteristics (Gao, 2017; Li et al., 2017; Ren, 1995), mineralization material source (Li Y J et al., 2017; Li Z Y et al., 2014) and ore genesis (Li, 2013; Wang, 2010; Li et al., 2006a; Qi et al., 2004; Wei, 2000; Liu and Zhang, 1996; Ren, 1992; Xu, 1991). However, it is still a matter of considerable debate in terms of ore-forming age, source of ore-forming fluid and metals, and ore genesis. Firstly, the ore-forming age includes two views: Indosinian (Nie et al., 2007) and Yanshanian (Li, 2016; Li Z Y et al., 2014; Liu and Zhang, 1996) mineralization. Even though it is considered to be Yanshanian mineralization, the specific ore-forming ages are quite different from each other. Secondly, the source of ore-forming fluid includes post-magmatic hydrothermal fluid, regional metamorphic hydrothermal fluid and meteoric hydrothermal fluid. Finally, there are also several different views on the genesis of the deposit, including: (1) epithermal hydrothermal deposit related to continental subvolcanic cryptoexplotion (Li Y J et al., 2017; Wang, 2010; Li J M et al., 2006a), (2) hot-spring type deposit (Liu and Zhang, 1996), (3) deep-source hydrothermal fluid cryptoexplotion-metasomatism deposit (Wei, 2000), and (4) metamorphic (hydrothermal) differentiation or ductile shear mylonite type Ag-Pb-Zn deposit (Ren and Cao, 1995).

In this paper, we report data of fluid inclusions, stable isotopes (H-O-S) and fluorite Sr-Nd isotopes, aiming to constrain the timing of ore mineralization, the source of the ore-forming fluid and metals, and the mechanisms of mineral

![Figure 1](image_url)

**Figure 1.** (a) Sketch map of the NCC showing the distribution of major Pb-Zn-Ag deposits (modified after Li and Santosh, 2014; Santosh et al., 2010); (b) regional geological map of the North Hebei showing the distribution of silver-polymetallic deposits (modified after Yang S D, 2000).
precipitation. Based on these studies, we develop a genetic model of the Niujuan-Yingfang Pb-Zn.Ag deposit, which can be used to guide prospecting and exploration.

1 GEOLOGICAL SETTING

A 1,500 km-long EW-trending Ag-Au-Pb-Zn belt (also known as Yan-Liao mineralization belt) occurs along the northern margin of the NCC, which hosts a metal resource of ca. 1,000 tons of Au and 20 million tons of Pb-Zn (Fig. 1; Zeng et al., 2020; Cook et al., 2009; Mao J W et al., 2005; Yang et al., 2003; Hart et al., 2002). Most of the polymetallic deposits are located in the Inner Mongolia uplift defined by the Junggar-Hegen fault zone to the north and the Fengning-Longhua fault to the south (Wang et al., 2018; Hart et al., 2002).

The NCC consists of the Archean to Early Proterozoic metamorphic basement complexes and the Proterozoic, Paleozoic, Mesozoic, and Cenozoic cover rocks (Zeng et al., 2020). The Archean to Early Proterozoic high-grade metamorphic complexes are composed of mafic granulite, amphibolite, gneiss, magnetite quartzite, marble, and charnockite (Su et al., 2015; Dong et al., 2013; Nie et al., 2002; Nie, 1997; Gao and Gao, 1988). The Paleoproterozoic metamorphic sequences comprise mainly schist, slate, shale, and psammite (Zeng et al., 2020). The cover rocks contain the Late Proterozoic and younger sedimentary rocks, comprising sandstone, conglomerate, coal-bearing shale, clastic rocks and carbonate (Nie, 1997). The Paleoproterozoic Hongqiyiqui Group is a set of volcanic sedimentary rocks with low amphibolite facies, and mainly comprises various kinds of granulite, with the central part marked by graphite-rich granulite, amphibolite, quartzite and marble assemblages (Wang, 1992).

Mafic to felsic granitoid batholiths, stocks and dykes are widespread around the northern NCC, especially the Phanerozoic granitoids (Zeng et al., 2020; Zhao et al., 2010; Hart et al., 2002). The Early–Middle Devonian alkaline complexes with emplacement ages ranging from 410–380 Ma in the northern NCC are probably related to the extension after collision between the NCC and the Bainaimiao arc terrane (Zhang et al., 2007a). Typical Devonian intrusions mainly include the Shuiquanou alkaline complexes in Zhangjiaokou (with an emplacement age of ~390 Ma; Luo et al., 2001), the Gushan monzodiorite in Chengde (with an emplacement age of 390±5 Ma; Zhang et al., 2007a), and the Chehugou syenite porphyry with an emplacement age of 376±3 Ma in Chifeng (Liu et al., 2010). An Andean-style continental arc was developed in the northern margin of the NCC due to the subduction of the Paleo-Asian oceanic plate beneath the northern NCC in the Late Carboniferous (Zhang et al., 2009a, b, 2007b). Numerous suites of Late Carboniferous–Middle Permian gneissic diorite-granodiorite intrusions with emplacement ages ranging from ~320 to 270–260 Ma are the geological records of Late Paleozoic magmatic arc (Wang et al., 2007). Final closure of the Paleo-Asian Ocean and collision between the Mongolian arc terrane and NCC occurred during the Late Permian to Early Triassic, followed by the post-collisional magmatism at ca. 250 Ma (Liu et al., 2010; Zhao et al., 2010; Chen et al., 2009, 2000). The northern margin of the NCC was intruded by numerous alkaline rocks and diorite dikes in the Late Triassic Period, which indicates an extensional setting after the collision (Mu et al., 2001; Han et al., 2000; Mu and Yan, 1992). The Jurassic–Cretaceous granitic and volcanic rocks are distributed widely along the northern NCC, coincidence with the large-scale lithospheric extension and crust-mantle interaction owing to the subduction of the Paleo-Pacific Plate (Zhu et al., 2015; Zeng et al., 2012; Dai et al., 2006).

The Ag-polymetallic mineralization in the northern NCC is common, and mostly associated with Mesozoic acid-intermediate acid magmatic rocks (Duan et al., 2008). The Mesozoic Ag-polymetallic mineralization is mainly characterized by metasomatism, hydrothermal filling and metamorphic hydrothermal mineralization related to the Yanshanian magmatism, as well as the transformation and reconstruction of ore deposits or source beds formed earlier, leading to the formation of various mineralization type including porphyry, skarn, magnatic hydrothermal vein and tectonic altered rock type. Typical deposits include the Bajiazi, Caijiaying, Yingfang, Daxigou, Wanquansi and Beichagoumen deposit (Liu Q M et al., 2018; Li and Zhang, 2011; Duan et al., 2008; Wang, 2008; Li et al., 2006b; Yang and Tian, 1998; Huang et al., 1997). These deposits are mainly distributed in the transition zone between continental volcanic-sedimentary basin and the Yanshanian magmatic belt, with volcanic-subvolcanic hydrothermal silver deposits as the main type, and the ore-forming ages are concentrated in the Middle–Late Yanshanian Period (Li et al., 2006b).

2 ORE DEPOSIT GEOLOGY

The Niujuan-Yingfang Pb-Zn.Ag deposit is located in the contact zone between the NNE-trending Shuanghuangqi-Wulonggou tectono-magmatic belt and the Guyuan fault-depression basin in the northern margin of NCC (Fig. 2a). More than 30 orebodies have been discovered in this deposit. The northern part of the deposit is the Niujuan silver-gold orebody, while the southern part is the Yingfang silver-lead-zinc orebody (Fig. 2b).

The basement rocks exposed in the vicinity of the deposit are the Paleoproterozoic Hongqiyiqui Group metamorphic rocks, including graphite biotite plagioclase gneiss, garnet biotite plagioclase gneiss, amphibolite, migmatisic gneiss and marble. The Hongqiyiqui Group metamorphic rocks were intruded by the Permian medium-coarse-grained biotite monzogranite and fine-grained biotite K-feldspar granite, as well as some felsic and diabase dykes (Yang et al., 2019), and the Niujuan-Yingfang Pb-Zn.Ag orebodies are mainly hosted in the Permian biotite monzogranite (Figs. 2f, 3). The fine-grained K-feldspar granite occurs as a stock to the west of the deposit, intruding into the monzogranite (Fig. 3). The Hongqiyiqui Group metamorphic rocks are covered unconformably by the Mesozoic Upper Jurassic–Lower Cretaceous volcanic rocks that are distributed in the NE-trending volcanic fault basins and consist of dacite, andesite, rhyolite and rhyolitic tuff (Nie et al., 2007). The Yanshanian intrusions are represented by the Late Jurassic Zhangjiaokou Period and Early Cretaceous Dabeigou Period (Niu et al., 1996), with the former mainly being granitic porphyry, quartz syenitic porphyry and monzonitic porphyry and the latter granite, granodiorite and quartz syenitic porphyry.
More than 20 faults and 10 circular structures have been discovered around the ore deposit, which constitute the structure of the mesh weaving pattern (Li and Wang, 2002). The Kangbao-Weichang EW-trending deep fault, Fengning-Longhua NE-trending concealed fault and Shanghuangqi-Wulonggou NNE-trending deep fault are located in the north, west and east of the mining area, respectively. The three deep faults and their secondary fault fracture zones are not only the dividing lines of tectonic-stratigraphic units, but also the migration channels of magma and related ore-forming fluids (Nie et al., 2007). The Niujuan-Laohuba fault fracture zone (F1 fault), which runs through the central zone of the mining area, is part of the Shanghuangqi-Wulonggou deep fault and has a close spatial relationship with the Niujuan-Yingfang deposit.

There are 26 orebodies of economic significance (10 silver and 16 gold orebodies) in the Niujuan Ag-Au deposit. The number 1 orebody is the main orebody, accounting for 92% of the silver metal content, and occurs as lenses or dikes of 40–450 m long and 0.73–8.1 m thick with 180–350 m down-dip extensions (Shen et al., 2012; Nie et al., 2007). Four orebodies were enclosed in the Yingfang deposit. The orebodies are cystic or lens-shaped, with small strike length. The largest orebody is 350 m long and 40–150 m depth (Shen et al., 2012). Both of the orebodies from two parts are controlled by the F1 fault (Fig. 3a). The fault/fracture zone is 8 km in length and 10–40 m in width, with striking 25º–35º and dipping 52º–65º SE (Wei, 2000), and comprise mainly silicified breccia and fault gouge (Wang et al., 2018).

The metallic minerals in the deposit are mainly pyrite, sphalerite, galena, with minor chalcopyrite, arsenopyrite,
pyrrhotite, argentite, native silver, tetrahedrite, pyrargyrite etc. The gangue minerals mainly include quartz, chalcedony, fluorite, sericite, chlorite and carbonates (Nie et al., 2007).

The hydrothermal alteration of the deposit is widespread and strong, and dominated by silicification, chloritization and sericitization (Wang et al., 2018; Li et al., 2017; Nie et al., 2007). The hydrothermal alteration shows compositional and textural zoning (Fig. 3). As the main ore-bearing unit, the silicification zone is distributed in the core, and the alteration mineral assemblages are quartz, chalcedony and minor sericite. Further outward from the core is the sericitization zone that is much wider than the silicification zone, formed in the breccia and the granite pluton and composed of sericite and subordinate hydromica and chalcedony. The granite pluton near the orebodies shows intense chloritization, with chlorite as the main altered mineral. Wang et al. (2018) observed an intimate genetic link between the composition of chlorite and mineralization center through EMPA and LA-ICP-MS studies on 21 samples of chlorite and biotite with different depths from 4 drill holes, which is potential for prospecting and exploration of such medium-low temperature hydrothermal vein type Pb-Zn-Ag polymetallic deposits.

According to the mineral paragenesis and vein crosscutting relationship, the mineralization processes can be divided into three stages: (1) pre-ore stage, with siliceous-chlorite-pyrite, (2) syn-ore stage, with quartz-silver-galena-sphalerite polymetallic sulfide, and (3) post-ore stage, with widespread fluorite and carbonate. Hand specimen photographs and microphotographs of representative samples from the Niujuan-Yingfang Pb-Zn-Ag deposit are shown in Fig. 4 and Fig. 5, respectively. Paragenetic sequences of minerals are shown in Fig. 6. Brief descriptions for the three stages were given below.

(1) Stage I is characterized by the occurrence of silicified breccia and quartz-chlorite-pyrite vein in the host granites. Rubbles of the breccia comprise the granite, early silicic aggregation and debris of quartz and feldspar with irregular shape. Cement of the breccia is composed mainly of the chalcedony and microcrystalline quartz. The quartz-chlorite-pyrite veins mainly comprise aphanitic quartz, chalcedony and disseminated idiomorphic pyrite. These veins basically cut through siliceous breccia and medium-coarse-grained monzogranite, with width up to 2 cm. Quartz and chlorite contents vary significantly in different veins. Sparsely disseminated pyrite generally is coupled with chlorite and distributed at the edge of veins. (2) Stage II is represented by the occurrence of abundant sulfides, mainly consist of pyrite, sphalerite, galena, arsenopyrite and chalcopyrite. Ag-bearing minerals precipitated at the end of this stage, as indicated by the metasomatic phenomenon of sphalerite and galena by pyrargyrite and tetrahedrite. (3) Stage III is symbolized by the occurrence of plentiful fluorite and calcite. The fluorite and calcite are always interwoven with the early mineral assemblages. Three sub-stages can be identified according to the color of fluorite, including purple fluorite, green fluorite and white fluorite sub-stage in turn.

3 SAMPLES AND ANALYTICAL METHODS

3.1 Fluid Inclusions (FIs)

Petrographic observation was done on samples from different stages at room temperature, and the target minerals are mainly quartz, sphalerite, fluorite and calcite.

Microthermometry measurement was implemented utilizing the Linkam MDS-600 heating-freezing stage (ranging from -196 to 600 °C) coupled with a ZEISS microscope at the Ore-forming Fluid Lab of School of Resources and Environmental Engineering, Hefei University of Technology. The accuracy of measurements was within ±0.1 °C, and the freezing-
heating rates were 0.2–5 ºC/min. However, when approaching a phase transition the rate dropped to 0.1–0.5 ºC/min. The measurements include (1) final ice melting temperature ($T_{m, \text{ice}}$), (2) melting temperature of the carbonic phase ($T_{m, \text{CO}_2}$), (3) melting temperature of the clathrate ($T_{m, \text{clath}}$), (4) homogenization temperature of the carbonic phase to the liquid ($T_{h, \text{CO}_2}$), and (5) total homogenization temperatures of fluid phases ($T_{h, \text{tot}}$). Salinities were calculated using the equations of Bodnar (1993) for aqueous (NaCl-H$_2$O) inclusions, and of Collins (1979) for CO$_2$-bearing inclusions.

Fluid inclusions (FI) laser Raman spectroscopy analysis was performed at the Institute of Geo-Fluids, School of Earth Science and Engineering, Nanjing University, using the Renishaw RM-2000 Raman microscope. This instrument records peaks in the range of 100–4 000 cm$^{-1}$ full-band with a resolution of 1–2 cm$^{-1}$, and the laser beam spot size was about 1 μm. Detailed parameters of the instrument can consult Ke et al. (2017).

### 3.2 Stable Isotopes

A total of 25 sulfides from stage II were selected for sulfur isotope analyses. Sulfur isotopes were measured on a $\Delta V$ plus mass spectrometer (Robinson and Kusakabe, 1975), using the VCDT standard at the Analytical Center of the Beijing Institute of Geology for Nuclear Industry. The analytical accuracy and precision are within ±0.2‰.

Hydrogen and oxygen isotope analyses were performed via a MAT-253 mass spectrometer in the same Analytical Center. The hydrogen isotopes were analyzed directly on FIs in quartz, while the oxygen isotopes were released from quartz by reacting with BrF$_5$. Detailed procedures can refer to Clayton and Mayeda (1963). The analytical precision for hydrogen and oxygen isotopes is within ±2‰ and ±0.2‰, respectively.

### 3.3 Sr-Nd Isotopes

A total of 9 basement metamorphic rocks (including 4 amphibolite and 5 gneiss), 3 volcanic rocks (including granite...
Figure 5. Microphotographs of representative samples from the Niujuan-Yingfang Pb-Zn-Ag deposit. (a) Silicified breccia; (b) quartz and feldspar fragments in silicified breccia; (c) quartz-pyrite vein cuts through early feldspar; (d) quartz-silver polymetallic sulfide stage; (e) early idiomorphic arsenopyrite is replaced by galena; (f) chalcopyrite is dissolved in sphalerite to form a solid solution separation structure; (g)–(h) late fluorite-calcite cements or cuts quartz-sphalerite vein; (i) argentite and pyrargyrite replace galena; (j) pyrargyrite vein cuts through sphalerite and galena; (k) electron probe energy spectrum of argentite; (l) electron probe energy spectrum of pyrargyrite. Qz. Quartz; Kfs. K-feldspar; Py. pyrite; Sp. sphalerite; Gn. galena; Apy. arsenopyrite; Ccp. chalcopyrite; Td. tetrahedrite; Pyr. pyrargyrite; Ser. sericite; Cal. calcite; Fl. fluorite.

porphyry, rhyolite and andesite) and 15 fluorite samples were selected for Sr-Nd isotope analyses. Sr-Nd isotope analyses were carried out on the Thermo-Finnigan TRITON TIMS at Tianjin Institute of Geology and Mineral Resources, China Geological Survey. Contents of Sm and Nd for fluorite were measured using the isotope dilution method with the uncertainty <0.5%. The Sr and Nd isotopic ratios were normalized against $^{87}\text{Sr}/^{86}\text{Sr}=0.1194$ and $^{146}\text{Nd}/^{144}\text{Nd}=0.7219$, respectively. The BCR-2 standard yielded Sm=6.578 ppm, Nd=28.86 ppm, $^{143}\text{Nd}/^{144}\text{Nd}=0.512644\pm 0.000004(2\sigma)$, $^{87}\text{Sr}/^{86}\text{Sr}=0.70496\pm 0.000007(2\sigma)$, consistent with the report by Bell et al. (1989). Sm-Nd isochron and Rb-Sr isochron age was calculated utilizing ISOPLOT software (Ludwig, 2003).

4 RESULTS
4.1 Fluid Inclusions (FIs)
4.1.1 Fluid inclusion petrography

Four types of FIs were identified in the quartz, sphalerite, fluorite and calcite from the Niujuan-Yingfang deposit (Fig. 7), as bellow.

(1) L$_0$-type FIs are the main type among different stages. The FIs which are mostly negative-crystal shaped (Figs. 7a, 7b, 7c) with sizes ranging from 5 to 15 μm, contain a liquid phase occupying 70 vol%–90 vol% of the inclusion. The host minerals are quartz (Figs. 7a, 7b), sphalerite (Fig. 7c), galena; Apy. arsenopyrite; Ccp. chalcopyrite; Td. tetrahedrite; Pyr. pyrargyrite; Ser. sericite; Cal. calcite; Fl. fluorite.

(2) V-type FIs are mainly recognized in quartz of the stage II, and the vapor occupies 70 vol%–90 vol% of the inclusion. These FIs are commonly negative-crystal and oval with sizes of 5–10 μm. Mostly, the symbiosis of V-type and L$_0$-type FIs in
the same visual field is common under the microscope (Fig. 7b), which may indicate fluid boiling.

(3) L₃-type FIs comprise vapor, liquid and solid phase, and accidentally occur in quartz of the stage II (Fig. 7c). Daughter minerals in such FIs are mainly halite.

(4) C-type FIs are three phases (VCO₂+LCO₂+LH₂O) with the typical double eyelid feature, and are generally distributed in quartz (Fig. 7a) and sphalerite (Fig. 7d) of the stages I–II. Carbonic phase accounts for 10 vol%–45 vol% of the inclusion. Such type of FIs is relatively common, and accounts for ~20% of the totality.

4.1.2 Fluid inclusion microthermometry

The microthermometric results are summarized in Table 1 and shown in Fig. 8.

(1) Quartz of the stage I: A total of 16 FIs were measured, and most of them were L₄-type. These FIs have Tₘ,ice ranging from 317.2 to 262.3 °C, Tₘ,ice ranging from -4.0 to -0.6 °C, and calculated salinities from 1.05 wt.% to 6.45 wt.% NaCl equiv. The C-type FIs yielded Tₘ,CO₂ ranging from -57.3 to -56.8 °C; Tₘ,fluid shows a range from 7.3 to 8.0 °C, with calculated salinities of 4.0 wt.%–5.2 wt.% NaCl equiv. The Tₘ,ic of these FIs are between 309.2 and 271.7 °C.

(2) Quartz, sphalerite and fluorite of the stage II: 53 FIs from syn-ore stage were measured. The L₄-type FIs in quartz, sphalerite and fluorite have Tₘ,ice from -3.7 to -0.8 °C, from -2.2 to -0.8 °C, and from -2.3 to -0.7 °C, with calculated salinities range from 1.4 wt.% to 6.0 wt.% NaCl equiv. from 1.4 wt.% to 3.7 wt.% and from 1.2 wt.% to 3.9 wt.% NaCl equiv., respectively. Tₘ,ic of these three minerals are from 278.3 to 228.7 °C, from 288.8 to 251.3 °C, and from 257.1 to 192.3 °C, respectively. The V-type FIs in quartz were homogenized to vapor at temperatures of 286.7–231.4 °C, with Tₘ,ice between -2.0 and -0.7 °C, corresponding to salinities of 1.2 wt.%–3.4 wt.% NaCl equiv. The C-type FIs in quartz and sphalerite yielded Tₘ,CO₂ ranging from -57.1 to -56.7 °C and -57.3 to -56.8 °C. Tₘ,clath of these FIs have a range of 7.3 to 8.3 °C and 7.2 to 8.0 °C, corresponding to salinities of 3.4 wt.%–5.2 wt.% and 4.0 wt.%–5.4 wt.% NaCl equiv. The Tₘ,ic of these FIs are from 292.3 to 258.2 °C and from 297.1 to 269.3 °C, respectively.

(3) Fluorite and calcite of the stage III: Fluorite and calcite from stage III contain vast L₄-type FIs. Tₘ,ice of L₄-type FIs in fluorite and calcite are from -2.4 to -0.4 °C, and from -1.1 to -0.4 °C. Tₘ,ic of fluorite and calcite are from 248.1 to 158.2 °C, and from 192.3 to 151.2 °C, respectively. The calculated salinities show a range of 0.7 wt.%–4.0 wt.% and 0.7 wt.%–1.9 wt.% NaCl equiv. for FIs in fluorite and calcite, respectively.

4.1.3 Laser Raman spectroscopy

Typical FIs from the Niujuan-Yingfang deposit were carried out using the laser Raman spectroscopy to ascertain the composition of the gas. The results (Fig. 9) indicate that the gaseous phase of the L₄-type FIs and coexisting V-type FIs are dominated by H₂O with minor N₂. The gaseous phase of C-type FIs in stage II quartz contains vast CO₂. Hence, the FIs from the fluid should be regarded as the NaCl-H₂O-CO₂±N₂ system. The decrease of CO₂ content in the ore-forming fluid from stage II to III indicates that immiscibility or fluid boiling phenomenon characterized by CO₂ escape occurred (Chen Y J et al., 2007) (Fig. 7b), which is also coupled with the carbonatization alteration during the post-ore stage III.

4.2 Stable Isotopes

4.2.1 Sulfur isotopes

Sulfur isotope compositions were measured for 25 sulfides from the Niujuan-Yingfang deposit, and the results were compared with published data (Li Y J et al., 2017; Li J M et al., 2006a) (Table 2; Fig. 10). A total of 52 samples yielded δ⁸³⁴Sᵥ-ₐₕ values ranging from -1.3‰ to 6.3‰, with an average of 3.7‰. Specifically, the δ⁸³⁴Sᵥ-ₐₕ values of sphalerite, galena and pyrite are 1.8‰ to 6.3‰, -1.3‰ to 4.5‰, and 2.6‰ to 5.7‰, respectively.

4.2.2 Hydrogen and oxygen isotopes

Hydrogen and oxygen isotope data are listed in Table 3. The δ¹⁸Oₐₕ values of 21 samples (11 from this study, and the rest from literatures) have a range of 0.6‰ to 5.3‰ (average 2.9‰), and the δ¹⁸Dₐₕ values of 11 samples (4 from this study, and the rest from literatures) range from -130.8‰ to -98.7‰ (average -115.3‰). The calculated δ¹⁸Ofluid values of the ore-forming fluid using the equation from Clayton et al. (1972) range from -7.40‰ to -2.39‰, with an average of −4.44‰.

4.3 Sr-Nd Isotopes

Sr-Nd isotope data are listed in Table S1. Nine basement metamorphic rocks analyzed in this study yielded Rb and Sr concentrations of 27.0 ppm–147.5 ppm and 179 ppm–450 ppm, respectively. ⁸⁷Rb/⁸⁶Sr and ⁸⁷Sr/⁸⁶Sr ratios of these samples range from 0.318 3 to 2.057 5 and 0.719 435 to 0.768 847, respectively. These basement rocks have Sm and Nd concentrations of 2.36 ppm–12.70 ppm and 8.8 ppm–99.9 ppm, with ⁴⁷Sm/⁴⁴Nd ratios of 0.08–0.18. ¹⁴⁷Sm/¹⁴⁴Nd ratios range from 0.08–0.18. ¹⁴³Nd/¹⁴⁴Nd ratios range from 0.510 758 to 0.512 538.

Three volcanic rocks yielded Rb and Sr concentrations of 121.5 ppm–186.5 ppm and 138.0 ppm–186.5 ppm, respectively.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Mineral</th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Arsenopyrite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sphalerite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Galena</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chalcopyrite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Argentite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tetrahedrite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pyrargyrite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pyrite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chlorite</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Sericite</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Fluorite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Calcite</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 6. Paragenetic sequence of minerals from the Niujuan-Yingfang Pb-Zn-Ag deposit.
$^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of these samples range from 0.699 1 to 3.162 9 and 0.708 222 to 0.716 337, respectively. These basement rocks have Sm and Nd concentrations of 3.80 ppm–9.59 ppm and 19.9 ppm–60.3 ppm, with $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of 0.10–0.12. $^{143}\text{Nd}/^{144}\text{Nd}$ ratios range from 0.511 762 to 0.511 854.

Fifteen fluorite samples have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ranging from 0.715 559 to 0.718 958. Ten fluorite samples yielded Rb and Sr concentrations of 0.069 ppm–10.5 ppm and 176 ppm–298 ppm, respectively, with $^{87}\text{Rb}/^{86}\text{Sr}$ ratios of 0.000 7–0.137 2. The fifteen fluorite samples yielded Sm and Nd concentrations of 1.03 ppm–8.45 ppm and 2.71 ppm–16.73 ppm, respectively (Table S1). $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of these fluorite samples range from 0.179 2 to 0.325 2, and the significant variations of these values allow a precise Sm-Nd isochron age to be obtained. These samples yielded a Sm-Nd isochron age of 158±35 Ma and an initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.511 607±0.000 056 (Fig. 11a).

5 DISCUSSION
5.1 Timing of Pb-Zn-Ag Mineralization

Previous studies on the timing of Pb-Zn-Ag mineralization from the Niujuan-Yingfang deposit yielded significantly varied age data based mainly on the Ar-Ar, K-Ar, and Rb-Sr isotopic systems. Liu and Zhang (1996) obtained an age of 120.7±3.2 Ma for a chalcedony sample from the crypto-explosive siliceous breccia by the whole-rock K-Ar method. Nie et al. (2007) chose K-feldspar from the fine-grained K-feldspar granite stock and ore-bearing crypto-explosive breccia dyke for $^{40}\text{Ar}/^{39}\text{Ar}$ isochron dating, and obtained two stage ore-forming ages of 227.9±4.8 and 216.7±6.1 Ma, respectively. Li Z Y et al. (2014) obtained a Rb-Sr isochron age of 154.1±2.6 Ma for sulfides ( sphalerite and paragenetic mineral assemblage of pyrite and galena) from the Niujuan Ag-Au deposit, suggesting that the mineralization was related closely to the Late Jurassic magmatism. Li (2016) also obtained a Rb-Sr isochron age of
**Figure 8.** Histograms of homogenization temperatures and salinities of fluid inclusions from the different stages of the Niujuan-Yingfang Pb-Zn-Ag deposit.

**Table 1** Summary of microthermometric data of the fluid inclusions in the Niujuan-Yingfang Pb-Zn-Ag deposit

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Type</th>
<th>Number</th>
<th>(T_{m, CO_2}) (°C)</th>
<th>(T_{m, ice}) (°C)</th>
<th>(T_{m, clath}) (°C)</th>
<th>(T_{h, CO_2}) (°C)</th>
<th>(T_{h, tot}) (°C)</th>
<th>Salinity (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I Quartz</td>
<td>L₀</td>
<td>11</td>
<td>-4.0–-0.6</td>
<td>262.3–317.2</td>
<td>1.1–6.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>5</td>
<td>-57.3–-56.8</td>
<td>7.3–8.0</td>
<td>29.9–31.1</td>
<td>271.7–309.2</td>
<td>4.0–5.2</td>
<td></td>
</tr>
<tr>
<td>II Quartz</td>
<td>L₀</td>
<td>17</td>
<td>-3.7–-0.8</td>
<td>228.7–278.3</td>
<td>1.4–6.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>8</td>
<td>-57.1–-56.7</td>
<td>7.3–8.3</td>
<td>29.3–31.1</td>
<td>258.2–292.3</td>
<td>3.4–5.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>V</td>
<td>8</td>
<td>-2.0–-0.7</td>
<td>231.4–286.7</td>
<td>1.2–3.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sphalerite</td>
<td>L₀</td>
<td>6</td>
<td>-2.2–-0.8</td>
<td>251.3–288.8</td>
<td>1.4–3.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>4</td>
<td>-57.3–-56.8</td>
<td>7.2–8.0</td>
<td>30.2–31.1</td>
<td>269.3–297.1</td>
<td>4.0–5.4</td>
<td></td>
</tr>
<tr>
<td>Fluorite</td>
<td>L₀</td>
<td>10</td>
<td>-2.3–-0.7</td>
<td>192.3–257.1</td>
<td>1.2–4.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III Fluorite</td>
<td>L₀</td>
<td>20</td>
<td>-2.4–-0.4</td>
<td>158.2–248.1</td>
<td>0.7–4.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td>L₀</td>
<td>5</td>
<td>-1.1–-0.4</td>
<td>151.2–192.3</td>
<td>0.7–1.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes: \(T_{m, CO_2}\)=melting temperature of the carbonic phase; \(T_{m, ice}\)=final ice melting temperature; \(T_{m, clath}\)=melting temperature of the clathrate; \(T_{h, CO_2}\)=homogenization temperature of the carbonic phase to the liquid; \(T_{h, tot}\)=total homogenization temperatures of fluid phases.
135.7±4.1 Ma for sulfides (sphalerite and galena) from the Yingfang Pb-Zn-Ag deposit.

Recently, the Sm-Nd isotopic compositions of hydrothermal calcic mineral assemblages (e.g., calcite and fluorite) have been used widely to constrain the timing of mineralization due to their relatively high REE concentrations and large ranges of Sm/Nd ratios (Zhang et al., 2015; Su et al., 2009; Peng et al., 2006). Halliday et al. (1990) for the first time used the Sm-Nd systems of fluorite to ascertain the timing of mineralization within the North Pennine ore-field of the UK, testifying that this is an effective approach to date the MVT deposits. By comparing the F-rich hydrothermal fluids between the Olympic Dam Fe oxide-Cu-U-Au-Ag deposit and Guilaizhuang gold deposit, Xu et al. (2015) considered that fluorine related to the formation of ore-bearing breccia was obviously associated with the mineralization, and obtained a precise ore-forming age of the Guilaizhuang deposit via fluorite-calcite Sm-Nd isochron. Here in this study, abundant fluorites occur in the siliceous breccia, coexisting with orebodies at the Niujuan-Yingfang deposit, suggesting an F-rich ore-forming hydrothermal fluid system. Considering that F is an effective ligand for migration of metals in ore-forming fluids like Cl-, OH- and HS- (Wood and Samson, 1998), ore-forming metals (e.g., Ag, Pb, Zn) could be precipitated substantially during the ascent of F-rich ore-forming fluids in breccia due to the change of physico-chemical conditions, and thus resulted in the mineralization and formation of fluorite as well in the late stage. Hence, the timing of Pb-Zn-Ag mineralization at the Niujuan-Yingfang deposit is best represented by the fluorite Sm-Nd isochron age of 158±35 Ma, which is contemporaneous with the Mesozoic Late Jurassic–Early Cretaceous volcanic-subvolcanic events in study area (Nie et al., 2007) but significantly younger than the host Late Permian granite plutons (Yan et al., 2019). This is comparable with previous studies yielding a Yanshanian mineralization event.

On the other hand, we attempted to calculate the Rb-Sr isochron of fluorites so as to compare it with the Sm-Nd isochron age. Unfortunately, as shown in Fig. 11b, no reliable Rb-Sr isochron age was obtained. This may be due to the following two reasons. Firstly, the overall low Rb contents of fluorites might lead to a relatively large error. Secondly, the closure of Rb-Sr isotope system is not well maintained after the formation of fluorite owing to the relatively open environment during the mineralization. This is also the reason why we cannot obtain a precise Sm-Nd isochron age.

In summary, the ore-forming age of the Niujuan-Yingfang Pb-Zn-Ag deposit can be represented approximatively by the fluorite Sm-Nd isochron age of 158±35 Ma within error.

5.2 Source of Ore-Forming Fluids

Generally, there are two possible origins for the ore-forming fluid of medium-low temperature hydrothermal vein type Pb-Zn-Ag polymetallic deposits: magmatic or metamorphic origin. Traditionally, the ore-forming fluid of hydrothermal vein type Pb-Zn-Ag deposits is ascribed to magmatic origin by many workers, and the mineralization is interpreted as the distal mineralization product of magmatic hydrothermal metallogenic system (Rottier et al., 2018; Catchpole et al., 2011; Cheilletz et al., 2002; Cunningham et al., 1996). Such deposits

Figure 9. Representative laser Raman spectra of different types of fluid inclusions from the Niujuan-Yingfang Pb-Zn-Ag deposit. (a) H₂O spectra of the vapor phase in L₀-type inclusion of quartz; (b) H₂O and N₂ spectra of the vapor phase in V-type inclusion of quartz; (c) CO₂ spectra of the vapor phase in C-type inclusion of quartz; (d) H₂O spectra of the vapor phase in L₀-type inclusion of fluorite.
usually do not exist alone, and the porphyry Cu-(Au) deposits and magmatic hydrothermal Sn deposits can be developed below them (Bendezú and Fontboté, 2009; Kamenov et al., 2002), and have a close genetic relationship with the intrusions and porphyry deposits (Catchpole et al., 2015; Rice et al., 2005). Sillitoe (2010) have proposed porphyry copper system, showing that magmatic hydrothermal system comprises a variety of different mineralization types, including porphyry mineralization, skarn mineralization and epithermal Pb-Zn-Ag mineralization. The epithermal Pb-Zn-Ag mineralization is mostly vein-type and controlled by fault tectonic belt, and the ore-forming fluid is dominated by meteoric water mixed with some amounts of magmatic fluid. The orogenic Pb-Zn-Ag deposits of metamorphic origin mainly occur in the metamorphic clastic rocks, and form in deep fault and its secondary fault (Li et al., 2010; Zhong et al., 2008; Chen et al., 2003). Lead, sulfur and carbon isotopes show that ore-forming materials derived mainly from the metamorphic rocks, and the study of hydrogen and oxygen isotopes indicates that the ore-forming fluid is mainly the mixture of deep metamorphic fluid and shallow meteoric water (Rubinstein et al., 2018; Paiement et al., 2012;
Beaudoin et al., 1992).

The Niujuan-Yingfang Pb-Zn-Ag deposit is probably not of magmatic origin. Arguments for this hypothesis are as follows. (1) The host granites show much older intrusive ages (268.7±3.2 Ma; Yan et al., 2019) than the timing of the Niujuan-Yingfang Pb-Zn-Ag mineralization (158±35 Ma), which thus could be excluded. (2) The nearby Yanshanian volcanic rocks (2–3 km away from the deposit; Fig. 2) are contemporaneous with the mineralization, and could be possible source of the ore-forming fluids. As shown in the Sr-Nd isotopic diagram (Fig. 12a), the fluorites (proxy for the ore-forming fluids) show basically different Sr-Nd isotopic compositions from those of the volcanic rocks, but they plot intermediate between the fields for the Yanshanian volcanic rocks and the country-rocks (the Paleoproterozoic basement rocks). It is possible that the Sr-Nd isotopic compositions of the

Table 3  Hydrogen and oxygen isotope compositions of fluid inclusions and quartz in the Niujuan-Yingfang Pb-Zn-Ag deposit

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mineral Stage</th>
<th>δ18O fluid (‰)</th>
<th>δD fluid (‰)</th>
<th>Data source</th>
</tr>
</thead>
<tbody>
<tr>
<td>YF-21</td>
<td>Quartz I</td>
<td>4.0</td>
<td>-12.89</td>
<td>N.D.</td>
</tr>
<tr>
<td>YF-22</td>
<td>Quartz I</td>
<td>1.4</td>
<td>-5.49</td>
<td>N.D.</td>
</tr>
<tr>
<td>YF-23</td>
<td>Quartz I</td>
<td>4.5</td>
<td>-2.39</td>
<td>N.D.</td>
</tr>
<tr>
<td>YF-24</td>
<td>Quartz I</td>
<td>3.2</td>
<td>-3.69</td>
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</tr>
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<td>YF-25</td>
<td>Quartz I</td>
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<td>-2.89</td>
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<td>YF-26</td>
<td>Quartz I</td>
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<td>-4.69</td>
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<tr>
<td>TC80</td>
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<td>-4.68</td>
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<tr>
<td>82CM3-1</td>
<td>Quartz I</td>
<td>4.2</td>
<td>-2.74</td>
<td>-105.0</td>
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<td>Quartz I</td>
<td>2.1</td>
<td>-4.76</td>
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</tr>
<tr>
<td>82CM3-3</td>
<td>Quartz I</td>
<td>1.3</td>
<td>-5.58</td>
<td>-98.7</td>
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<tr>
<td>ZK83-1</td>
<td>Quartz I</td>
<td>2.8</td>
<td>-4.11</td>
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<tr>
<td>ZK79-3</td>
<td>Quartz I</td>
<td>2.6</td>
<td>-4.27</td>
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<td>9-72-4</td>
<td>Quartz I</td>
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<td>-3.89</td>
<td>-119.4</td>
</tr>
<tr>
<td>9-78-2</td>
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<td>-5.56</td>
<td>-113.2</td>
</tr>
<tr>
<td>1-79-4</td>
<td>Quartz II</td>
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<td>-7.46</td>
<td>-104.3</td>
</tr>
<tr>
<td>JYF-12</td>
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</tr>
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<td>NJZ-45</td>
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<td>NJZ-49</td>
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<td>-6.56</td>
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<td>NJZ-54</td>
<td>Quartz II</td>
<td>1.1</td>
<td>-6.96</td>
<td>-128.3</td>
</tr>
</tbody>
</table>

Notes: N.D.~not determined; δ18O_{water} values are calculated based on the quartz-water equilibrium temperature formula provided by Clayton et al. (1972); Temperatures are based on microthermometric results of fluid inclusions.

Figure 11. Diagrams of Sm-Nd isochron and Rb-Sr isochron for the fluorites from the Niujuan-Yingfang Pb-Zn-Ag deposit.
Figure 12. Sr-Nd isotopic data of fluorites and associated granites in the vicinity of the Niujuan-Yingfang Pb-Zn-Ag deposit. Also shown for comparison are the Sr-Nd isotopic data of the Mesozoic volcanic rocks (Xia et al., 2016; Zhang et al., 2016; this study) and of the Hongqiyingzi Group metamorphic rocks (Wang et al., 2011; Liu et al., 2006; Hu et al., 1996; this study). Sr-Nd isotopic data of the host granites are from Yan et al. (2019).

5.2.1 Sr-Nd isotopic evidence

Fluorite Sr-Nd isotope composition in hydrothermal deposits is an important means to trace the source of ore-forming fluids (Zhang et al., 2015; Peng et al., 2003; Xu et al., 2003, 2001). The fluorites commonly have very low Rb/Sr ratios and high REE contents, which allow the Sr-Nd isotopic compositions of the source of ore-forming fluids to be determined easily (Zhang et al., 2015; Munoz et al., 2005; Sallet et al., 2000). We obtained the initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $\varepsilon^{148}\text{Nd}(158 \text{ Ma})$ values of fluorites in the ranges from 0.71556 to 0.71896 and from -16.8 to -15.5, respectively (Table S1). Such enriched Sr-Nd isotope characteristics indicate a crustal origin for the ore-forming fluids. As seen in Fig. 12a, the Sr-Nd isotopic compositions of the ore-forming fluids are in the Sr and Nd isotopic ranges for the Hongqiyingzi Group basement metamorphic rocks. This indicates that these basement rocks could be the source of ore-forming fluids for the Niujuan-Yingfang deposit.

5.2.2 H-O isotopic and fluid inclusion evidence

Hydrogen and oxygen isotope compositions of quartz can be used to constrain possible origin of the ore-forming fluids (Ma et al., 2019; Guo et al., 2019, 2014; Clayton et al., 1972). In order to obtain the characteristics of initial ore-forming fluids, we carried out H-O isotope analysis on the quartz from stages I and II (Table 3). In the plot of $\delta^{18}\text{D}_{\text{fluid}}$ vs. $\delta^{16}\text{O}_{\text{fluid}}$ (Fig. 13), our samples plot in the field between the fields for the primary magmatic/metamorphic fluids and the meteoric water line, and are close to the latter, suggesting that the ore-forming fluids contain large amounts of meteoric water. As discussed before, the Yanshanian volcanic rocks are less likely to provide ore-forming fluids, we thus suggest that the primary ore-forming fluids could be the metamorphic fluids derived from the Paleoproterozoic rocks, which mixed with meteoric water during ascent to shallow crustal levels. As seen in Fig. 13, our samples show a trend towards the meteoric water line from the stage I to II, revealing a significant involvement of meteoric water in the later stage. We suggest that the extensive involvement of meteoric water was probably related to the contemporaneous volcanic rocks that are expected to provide continued heat source, leading to the circulation and migration of meteoric water, and subsequent mixing with the deep-crustal ore-forming fluids.

In addition, the fluid inclusion data (Figs. 7, 8) are consistent with the metamorphic origin of ore-forming fluids. Metamorphic fluids are characterized by abundance of H$_2$O and CO$_2$ (Xiao et al., 2018), with H$_2$O originated mainly from the dehydration of hydrous phases and CO$_2$ mainly from the decarbonization of carbonate minerals during metamorphism in the deep crustal levels (Yang and Li, 2013; Fan et al., 2008). Abundant C-type FIs distributed in the quartz from stages I–II indicate
that the ore-forming fluids are enriched in CO₂, which agrees with a metamorphic origin for the ore-forming fluids.

5.3 Source of Ore-Forming Materials

The sulfur isotopic compositions of sulfides can offer meaningful insights into the source of sulfur in the ore-forming fluid and contribute to define the physicochemical conditions (e.g., pH, temperature, oxygen fugacity and ion activity) of metal precipitation in hydrothermal deposits (Yang et al., 2020; Ma et al., 2019; Liu W H et al., 2018; Ohmoto and Rye, 1979). The δ²⁴S V CDT values of sulfides from the Niujuan-Yingfang deposit range from -1.3‰ to 6.3‰ with an average of 3.7‰, showing a slightly positive sulfur isotopic feature compared to meteorite and mantle sulfur. In addition, sulfur isotope analyses demonstrate that the pyrite and sphalerite are enriched in heavy ³⁴S compared to galena in the stage II (Fig. 10), suggesting that the sulfides are in equilibrium with the fluid. Considering that the gap between the ore-forming age (158±35 Ma) and the intrusion age (268.7±3.2 Ma) of host medium-coarse-grained biotite monogranoenite (Yan et al., 2019), we suggest that the mineralization has no genetic relationship with these Permian granites. In terms of sulfur isotope, the δ²⁴S V CDT values of Sanggan Group and Qianxi Group from the adjacent area in North Hebei Province range from -0.04‰ to 3.4‰ and from -1.2‰ to 5.2‰, respectively (Wang, 2008), largely overlaying the mantle- source magmatic sulfur, which is owing to their protoliths being a set of ultrabasic-basic-intermediate-felsic igneous rocks. Here, the only reported δ³⁴S V CDT value of pyrite (10.5‰) in granulite from the Hongjiyingzi Group (Hu et al., 1990) cannot represent the whole sulfur isotope compositions because of the complex lithology. Given that the protoliths of biotite plagioclase gneiss are intermediate-basic volcanic lavas and clastic rocks (Shen et al., 2012), the δ³⁴S V CDT value of such rocks should likewise consist with the magmatic sulfur. Therefore, we believe that the sulfur in the ore-forming fluids at the Niujuan-Yingfang deposit might be inherited from the basement metamorphic rocks with minor magmatic source, which is also supported by Li et al. (2006a).

On the other hand, the northern margin of the NCC and adjacent areas belong to the high abundance geochemical background field of Ag, Au, Pb, Zn, Mo and other metallogenic elements. A large number of Pb-Zn-Ag deposits (e.g., Wangquansi, Lanyan, Caijiaying, Qingyanggou, Niujuan-Yingfang) and U-Mo deposits (e.g., Sadaigoumen, Beichagoumen) are distributed in this region (Shen et al., 2012). The basement metamorphic rocks represented by the Paleoproterozoic Hongjiayingzi Group are considered as the source of ore-forming metals (Ren, 1997). The concentrated Clark values of Ag, Pb and Zn in the Hongjiayingzi Group (7.05, 3.71 and 3.25) are significantly higher than those of the Mesozoic volcanic rocks (5.06, 2.09 and 0.88), and those of the Indosinan to Yanshanian granites (4.64, 3.08 and 1.00), suggesting that Paleoproterozoic metamorphic rocks may be the main source of metals in this area (Shen et al., 2012). Furthermore, some Pb-Zn deposits are even produced in the Hongjiayingzi Group directly (Shen et al., 2012; Mao et al., 2002; Ren, 1997).

To summarize, it is concluded that the basement metamorphic rocks, especially those with protoliths of intermediate-basic igneous rocks, may provide the major source of sulfur and metals for large-scale Pb-Zn-Ag mineralization in North Hebei region during the tectono-thermal activities in the Mesozoic. Ore-forming metals could be extracted from the source along with ore-forming fluid.

5.4 Mineral Precipitation Mechanism

As a rule, silver exists principally in the form of Ag⁺ in ore-forming fluids (Williams-Jones and Migdisov, 2014), and is transported dominated as silver bisulfide (AgHS⁻) and chloride (AgCl⁻) species (Stefánsson and Seward, 2003). Experimental studies have revealed that, at lower temperatures (<200 °C), AgHS⁻ predominate at near-neutral conditions, whereas AgCl⁻ are dominant under mildly acidic to acidic conditions (Gammons and Barnes, 1989; Seward, 1976). Conversely, at relatively high temperatures (>400 °C), silver is transported dominantly as a AgCl⁻ in the ore-forming fluids, whereas AgHS⁻ are only stable in basic conditions (Stefánsson and Seward, 2003; Gammons and Williams-Jones, 1995). The widespread sericitization in the Niujuan-Yingfang deposit suggests that the ore-forming fluid is near-neutral to weakly acidic (Ma et al., 2019). Considering that the fluids of the stage I and II are characterized by medium to low temperature (356 to 203 °C), it is probable that the silver was transported dominantly by AgCl⁻. Analogously, experimental studies demonstrate that, like silver, lead and zinc are transported mainly as chloride complexes of Pb²⁺ and Zn²⁺ in hydrothermal fluids (Ruaya and Seward, 1986).

Commonly, there are four mechanisms which will give rise to ore precipitation in hydrothermal deposits, including: (1) boiling, (2) cooling, (3) fluid mixing, and (4) fluid-rock interaction (Williams-Jones et al., 2010; Ulrich et al., 2002; Hezarkhani et al., 1999). Large-scale fluid boiling had taken place in the Niujuan-Yingfang deposit as evidenced by the existence of cryptoexplosive breccia, adularia and chalcedony (Ding, 2017), and particularly, the identification of boiling and immiscibility as revealed by the fluid inclusions of the stage II (Fig. 7b). The reason for metal precipitation caused by fluid boiling is the separation and dispersion of gases (e.g., H₂S, CO₂, HCl, HF). Firstly, the escape of gases significantly increases the concentration of metal elements in the fluid and decreases the solubility of metals in the fluid, leading to the supersaturated precipitation of metal minerals (Zhang, 1997; Cooke et al., 1996). On the other hand, the escape of acid gases tends to result in an increase of pH value of the fluid and of reduced sulfur concentration, which would consequently change the solubility of metal elements in the fluid and become an effective mechanism for the precipitation of metal elements migrated by chloride (Zhang, 1997). From the stage I to II, the salinities do not change dramatically (Table 1). However, the temperatures decrease remarkably along with the mineralization (Fig. 14). The drop of temperature can significantly influence the dissociation of metal chloride complexes; hence, the cooling might be one of the important factors for mineral precipitation at the Niujuan-Yingfang deposit. As shown before, the ore-forming fluid is composed of heated circulating meteoric water and metamorphic fluids, thus, fluid mixing might also have played a role in ore deposition (Fig. 14). In addition,
intense water-rock interaction did take place in this deposit. During the process of neutralization reaction, feldspars in the granites were altered to sericite and quartz, and increasing pH causes a marked decrease in H⁺ concentration in the ore-forming fluids, which plays an important role in the formation of deposit (Ma et al., 2019) illustrated by the following reactions e.g., Ag(HS)=S²⁻+H⁺+Ag⁺, 2Ag⁺+H₂S=Ag₂S+2H⁺, and 2Ag(HS)₂⁻⁻=Ag₂S+H₂S+2HS⁻⁻ (Shang et al., 2004; Gammons and Barnes, 1989). The relatively high pH value is also indicated by the precipitation of carbonates in the ore deposit. Therefore, water-rock interaction also played an important role in the formation of the Niujuan-Yingfang deposit.

To sum up, fluid boiling and cooling are the two important mechanisms for ore precipitation, and fluid-rock interaction is also indispensable. Relatively speaking, fluid mixing does not play a decisive role in the ore precipitation process.

5.5 Genetic Model

Combined with the ore deposit geology, mineralization age, fluid inclusions and isotope data, we proposed a genetic model for the formation of the Niujuan-Yingfang Pb-Zn-Ag deposit. The Pb-Zn-Ag mineralization in the northern NCC is in coincidence with the large-scale lithospheric extension and crust-mantle interaction owing to the subduction of the Paleo-Pacific Plate and the closure of the Mongol-Okhotsk Ocean during the Early Cretaceous (Liu et al., 2016; Ouyang et al., 2013; Zhu et al., 2011). Asthenosphere upwelling is expected to cause crustal thinning and reactivation of ancient fault systems, leading to the melting of lower crustal rocks and generation of voluminous magmas in the northern NCC, represented by the Zhangjiakou Formation in study area. Meanwhile, large-scale regional metamorphism occurred responding to the intense tectono-thermal activities, which is expected to occur contemporaneously with the Yanshanian magmatism but at shallower crustal levels (usually 15–20 km). Although these Yanshanian metamorphic rocks have not yet been exposed, deep metamorphic fluids can be transported for a long distance through fault zones or tectonic fracture zones (Boutoux et al., 2014; John et al., 2012; Walther and Orville, 1982). During the process of mid-crustal metamorphism, metamorphic fluids can be released due to dehydration of hydrous minerals such as mica, pyrophyllite, chlorite and serpentine, which is commonly accompanied by release of silica due to desilication under the conditions of high greenschist to amphibolite facies metamorphism. Such process also triggers the decarbonization due to the thermal decomposition of carbonate minerals (CaCO₃+ SiO₂→CaSiO₃+CO₂) and abundant K⁺, Na⁺, Ca²⁺ and Mg²⁺ and metallic elements such as Pb²⁺, Zn²⁺, Ag⁺ and Au⁺ can also be released into the metamorphic fluids, which leads to the silicification, K-feldsparization and carbonatization alteration (Chen Y J et al., 2007).

On the other hand, huge amount of heat carried by the voluminous magmas could cause the circulation and heating of percolating meteoric water, generating convective circulating pools. This kind of hot water accumulates in the center of deep heat source, and is unevenly mixed with the deep metamorphic fluids rich in volatiles and metals. Driven by the heat, the fluids constantly interact with the wall rocks (e.g., volcanic rocks, Permian granites and basement metamorphic rocks) in the process of outward diffusion along the fault zone, additionally increasing the contents of metals in the ore-forming fluids by extraction from the source rocks (mainly Hongqiyingzi Group basement rocks). When the overlying wall rocks prevent the fluids from moving upwards further, a large amount of fluids can gather at the leading edge of the fault and explode the overlying rocks, leading to the formation of cylindrical fractures which provide enough space for the further diffusion of the fluids. This results in fluid boiling due to the sudden drop of pressure. Such a process leads to the escape of volatiles, and increases the concentration of metals in the fluid, further causing the supersaturated precipitation of sulfide minerals. In addition, the escape of acid gases results in the increase of pH value of the fluid and the increase of reduced sulfur concentration, which also facilitated the precipitation of the ore minerals. Where after, with the drop of temperature of the fluid, a large number of ore minerals were deposited within extensional
structures and formed the large deposit.

Overall, the Niujuan-Yingfang deposit could be classified as a medium-low temperature hydrothermal vein-type Pb-Zn-Ag polymetallic deposits originated from metamorphic fluids.

6 CONCLUSIONS

(1) The fluorite Sm-Nd isotopic dating shows that the ore-forming age of Niujuan-Yingfang Pb-Zn-Ag deposit is 158±35 Ma within error, indicating a Middle–Late Yanshanian metallogenic event.

(2) H-O-S and fluorite Sr-Nd isotopes obtained from the Niujuan-Yingfang deposit prove that the ore-forming fluids are a mixture of deep metamorphic fluids and shallow meteoric water. The sulfur and metals originate mainly from Hong-qyingzi Group basement metamorphic rocks.

(3) Fluid boiling and cooling are the two major factors controlling the mineral precipitation. Moreover, water-rock interaction also contributed to the formation of the deposit.

(4) The Niujuan-Yingfang Pb-Zn-Ag deposit could be classified as a medium-low temperature hydrothermal vein-type Pb-Zn-Ag polymetallic deposits originated mainly from metamorphic fluids.

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