

## Article

# Rb–Sr Pyrite Dating and S–Pb Isotopes in the Fang'an Gold Deposit, Wuhe Area, Eastern Anhui Province

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**Abstract:** The Fang'an gold deposit in the Wuhe area, Anhui Province, is located in the area adjacent to the Bengbu Uplift and Wuhe Platform Depression in the southeastern part of North China. This study aimed to determine the deposit's mineralization age and the source of its metallogenic materials and mineralization processes through investigations into its geological characteristics, Rb–Sr isotopes, and S–Pb isotopes. The orebodies of the Fang'an gold deposit in the Neoproterozoic Xigudui Formation primarily exhibit a vein-type structure. The ore-forming process can be divided into four stages: (i) the quartz stage (Py1); (ii) the quartz–pyrite stage (Py2); (iii) the polymetallic sulfide stage (Py3); and (iv) the carbonate stage. Of these, the main mineralization stage is also the main period in which gold mineralization occurs. In situ sulfur isotope results of pyrite (Py1 to Py3) in the first three mineralization stages, suggesting a contribution of sulfur from crust–mantle magmatic fluids. The  $\delta^{34}\text{S}$  values for Py2 (average 5.51‰) are higher than Py1 (average 4.45‰) and showed that the magmatic fluids mixed with meteoric waters. The  $\delta^{34}\text{S}$  values for Py3 (average 5.18‰) are lower than Py2 (average 5.51‰), revealing that it related fluid immiscibility. The lead isotopic compositions of sulfides within the ores possessed  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios ranging from 16.759 to 16.93,  $^{207}\text{Pb}/^{204}\text{Pb}$  ratios ranging from 15.311 to 15.402, and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios ranging from 37.158 to 37.548. These lead data were plotted close to the Xigudui Formation, relatively distant from the Mesozoic granites, indicating that the Xigudui Formation was the source of lead for the Late Mesozoic ores of the deposit. Taken together, due to the degassing of mantle-derived magma in the shallow parts of the crust, it can be determined that the sources of ore-forming sulfur and lead were crust–mantle magmatic activities in the Wuhe area. Rb–Sr dating of pyrite from Fang'an gold deposit reveals that the mineralization occurred at  $126.89 \pm 0.58$  Ma. Considering the previous research into the dating of magmatic rocks in the Wuhe area, we propose that the genesis of the Fang'an gold deposit is closely associated with magmatic activities in the area at around 130 Ma.

**Keywords:** Fang'an gold deposit; Wuhe area; S–Pb isotopes; Rb–Sr isotope dating; mineralization age



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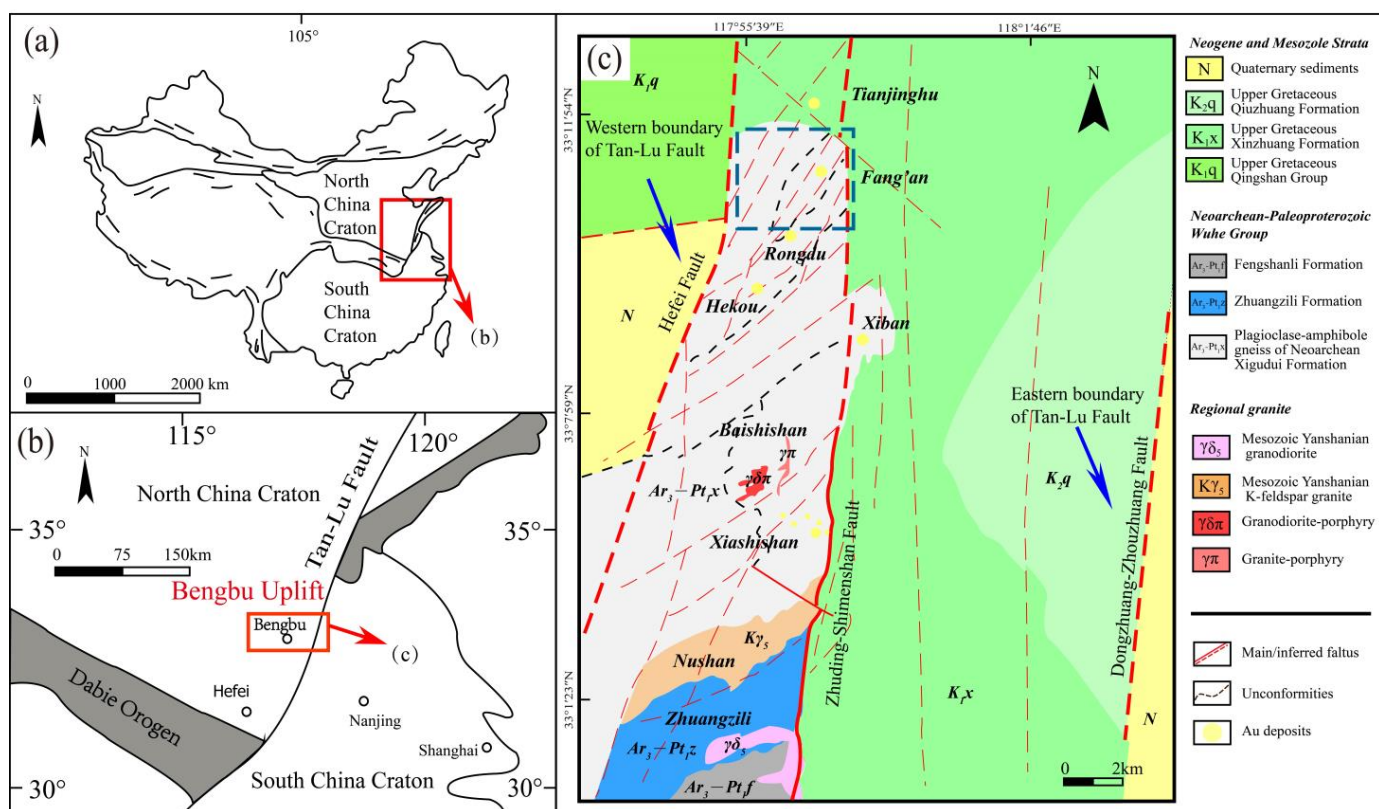


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## 1. Introduction

The Wuhe area is located on the southeastern margin of the North China Craton (NCC) (Figure 1a) and is adjacent to the Bengbu Uplift and the Wuhe Platform Depression [1,2]. This area is characterized by ductile and brittle–ductile tectonics and magmatic activity, which are favorable for mineralization [3]. To date, quartz–vein gold deposits occur in this area [4–9], including Dagongshan, Hekou, Rongdu, Zhu Ding, and Fang'an. Previous studies have been conducted on Wuhe gold deposits, contributing to the advancement of

gold mineralization theory and practical mineral prospecting in the area [4–12]. The Wuhe gold deposits are hosted in the Neoproterozoic Xigudui Formation [11]. This Formation is a source bed and provided ore-forming materials [13–15]. In addition, previous study of S isotope data for Wuhe gold deposits have shown that the ore-forming materials were derived from the mantle and wall rocks [14]. Recently, gold mineralization at Wuhe area has been generally constrained as 113–134 Ma corresponding to the Early Cretaceous as deduced from Rb–Sr, Re–Os, K–Ar, and Ar–Ar geochronology [4,5,7,9]. The ore-forming materials were related to the Early Cretaceous magmatism [5,9,16]. Despite many previous studies, the ore-forming materials sources remain debated in the Wuhe gold deposit, including mantle-derived materials, wall rock sources, and magmatic sources [4,5,9,13–16].



**Figure 1.** Geological map of the Wuhe area: (a) Schematic map of tectonic units in China; (b) tectonic location of the Wuhe area in eastern China; (c) geological map of the Fang'an gold deposit (modified after [4,13]).

The Fang'an gold deposit was first explored in 2018 by Geological Team 312 of the Anhui Geological and Mineral Exploration Bureau, China. Nevertheless, research on the geological characteristics of the Fang'an deposit and its mineralization process remains relatively limited. In this study, we present new Rb–Sr isotope data of pyrite with a view to elucidating the timing of magmatism and gold mineralization. Additionally, we present in situ results on the sulfur isotopes of pyrite and the lead isotopes of sulfide in order to identify the sources of the ore-forming materials. By combining our new results with the published data, we attempt to formulate the process of mineralization of the Fang'an deposit.

## 2. Geological Characteristics

### 2.1. Regional Geology

The Wuhe area is located at the intersection of the south margin of the NCC and the Qinling–Dabie orogenic belt (Figure 1b). The NNE-trending Tan–Lu Fault Zone (TLFZ) passes through this area, with the Bengbu Uplift to the west. The Wuhe area is mainly

covered by Quaternary sediments, and the exposed metamorphic basement comprises the Neoarchean–Paleoproterozoic Wuhe group (Ar<sub>3</sub>wh) (Figure 1c) with a total thickness of over 6400 m. Based on its lithological characteristics, the Wuhe group is divided into five subunits: the Xigudui, Zhuangzili, Fengshanli, Xiaozhangzhuang, and Yinjiajian Formations [17]. The Wuhe group is composed substantially of greenschist-to-granulite-facies metamorphosed flysch-type sedimentary rocks and volcanic rocks [8]. Tectonically, the complex is part of the NCC basement [18]. The Xigudui Formation is chiefly source bed in the Wuhe group, with the thickness (>1535 m) [14]. The Xigudui Formation primarily consists of amphibolite, amphibole plagioclase gneiss, and biotite plagiogneiss, which has undergone amphibolite facies metamorphism. Moreover, the Phanerozoic strata consist of the Cretaceous Qingshan Group (andesite), Xinzhuang Formation (clastic sediments), and Neogene–Quaternary sediments (Figure 1c).

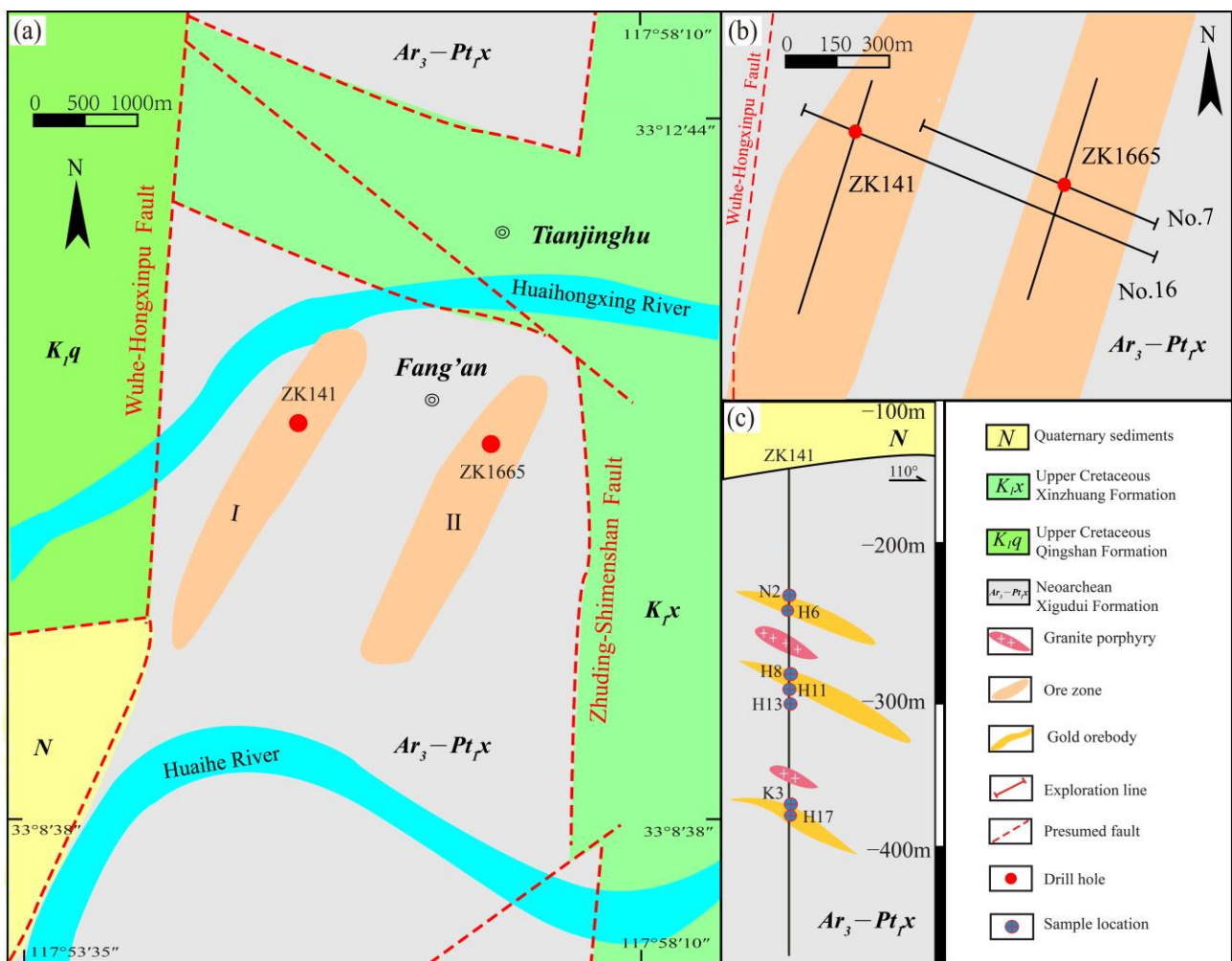
The granitic rocks exposed in the central-to-southern part of the study area primarily consist of granites, diorites, granodiorites, and potassic granites [19], such as the Shanzhangjia, Baishishan, Nvshan, and Zhuangzili plutons (Figure 1c). These granitic rocks show clear intrusive contact with the wall rocks (the Xigudui Formation). Only a few veins have been observed in the north of the study area. Yang et al. (2010) determined that the Zhuangzili Formation comprises potassic granite and granitic amphibolite with an emplacement age of 2.1 Ga [17]. The age of the Nvshan pluton is  $130.1 \pm 3$  Ma by zircon U–Pb dating analysis [20]. Wang et al. (2012) suggested that these magmatic intrusions are part of the metamorphic basement of the Xigudui Formation, with the remainder being products of Mesozoic magmatism [6] with an age of 120–160 Ma. Mesozoic intrusions in the Wuhe area have been divided into Late Jurassic and Early Cretaceous granitoids. Moreover, intermediate–acid and mafic dikes primarily occur in the forms of granite porphyry, granodiorite porphyry, lamprophyre, granodiorite porphyry, and diabase. The gold deposits in the Wuhe area are usually closely spatially related to Yanshanian magmatic veins [13]. The structures in the Wuhe area substantially comprise E- and NE-to-NNE-trending faults, with the nearly NNE-trending continental-scale TLFZ being the most important structure at the regional scale. The Hefei Fault and Dongzhuang–Zhouzhuang Fault mark its western and eastern boundaries, respectively (Figure 1c).

## 2.2. Deposit Geology

The Fang'an gold deposit located in the eastern Wuhe district (Figure 1b) [1,3], is a small-sized quartz vein-type deposit influenced by the Xigudui Formation and the NNE-trending fault structure. It contains gold reserves that are 2.269 tons, with an industrial grade of 3.67 g/t; lead reserves are 13.38 tons, with an average grade of 2.26%; silver reserves are 12.682 tons, with an average grade of 28.81 g/t.

Based on drill hole data, the Fang'an deposit is covered by the Quaternary sediments, with a depth of about 60.33–90.70 m. Strata in the Fang'an deposit consist of the Neoarchean Xigudui Formation, Late Mesozoic Qingshan and Xinzhuang Formations, and Quaternary sediments. The Fang'an deposit is located between the Wuhe–Hongxinpu fault and the Zhuding–Shimenshan fault (Figure 1c) [13], which are secondary faults of the TLFZ. Plutonic rocks, primarily composed of granitic porphyry, diorite porphyry, and diorite, have been identified within the Fang'an deposit through drill hole investigations.

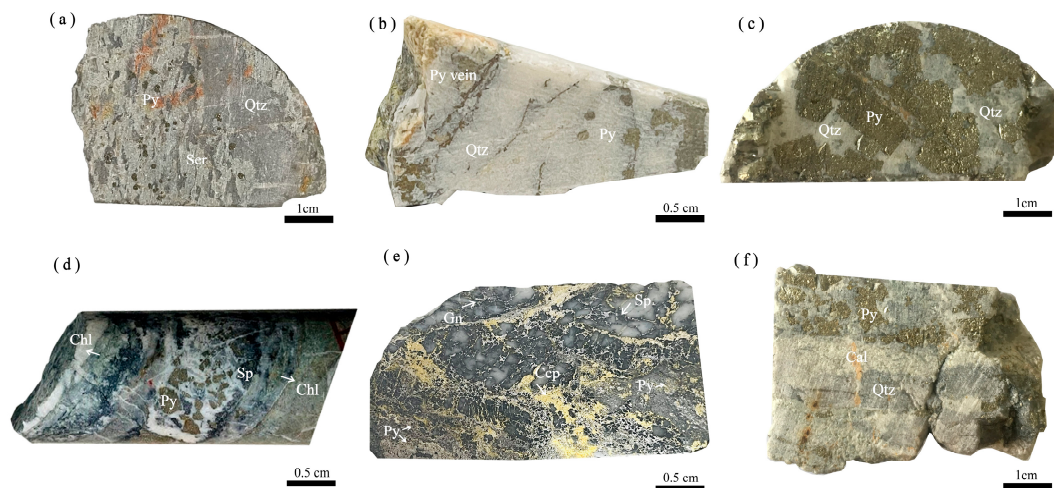
The Fang'an deposit comprises two ore zones, I and II (Figure 2a). The ore-bearing structures consist of ductile–brittle shear zones with nearly N–S strike and a SE dip at 30–60°. Gold-bearing quartz veins are primarily hosted within Xigudui Formation.



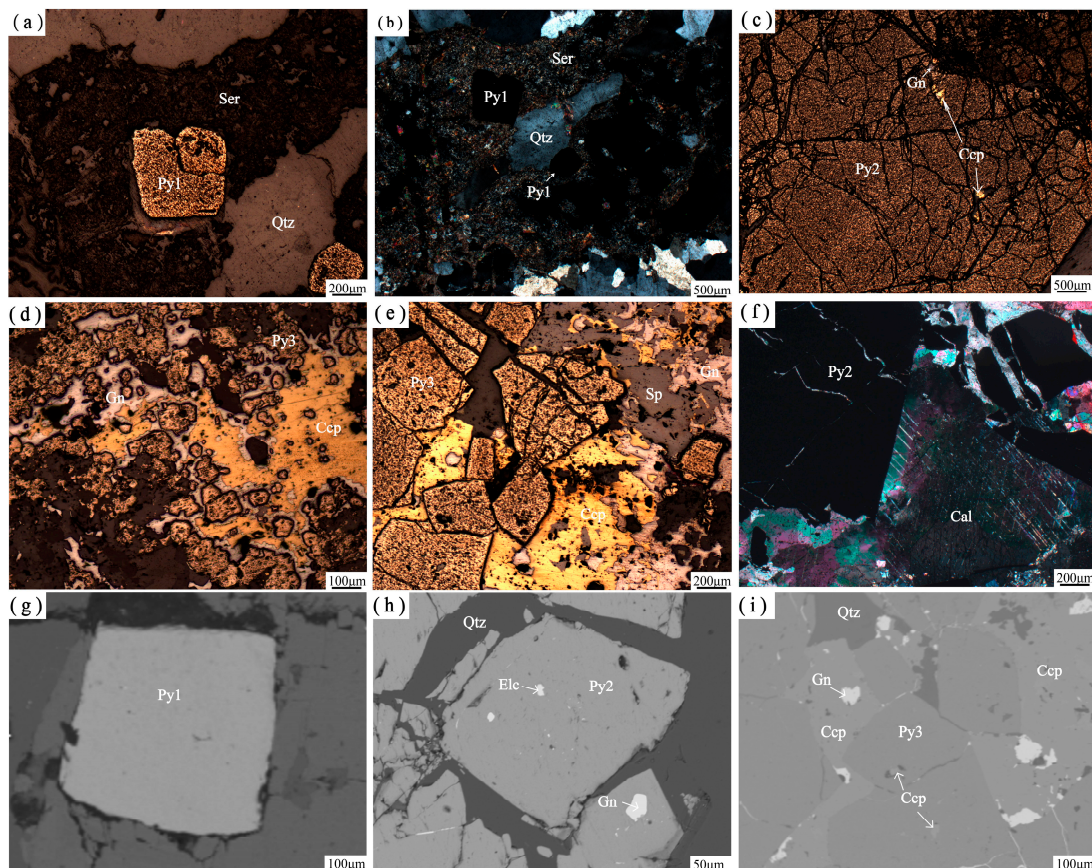
**Figure 2.** (a) Map of metallogenic belt distribution of Fang'an gold deposit, modified after [21]; (b) location of sampled drill holes projected onto the I metallogenic belt; (c) cross-section of No.16 exploration line in the Fang'an gold deposit.

The crosscutting and replacement relation of ore minerals and gangue minerals show different mineralization stages. The photographs of ore in Figure 3 show gold mineralization assemblages and alterations from the Fang'an deposit. The ore minerals are mainly pyrite, followed by halcopryrite, sphalerite, and galena (Figures 3 and 4). The gangue minerals primarily consist of quartz, calcite, and sericite. The wall rocks alterations are common in the Fang'an deposit, including pyritization, silicification, sericitization, chloritization, and carbonation (Figures 3 and 4), showing medium–low-temperature hydrothermal alteration combinations. The vein minerals are dominated by quartz and calcite.





**Figure 3.** Ore features of the Fang'an gold deposit: (a) sericite–quartz altered rocks; (b) pyrite–milky white quartz veins; (c,d) pyrite occurs as coarse euhedral cubes and as subhedral aggregates; (e) quartz, pyrite, and base–metal sulfide occur as veinlets and stockworks in disseminated ores; (f) calcite vein cuts through early minerals. Ccp—chalcopyrite; Py—pyrite; Sp—sphalerite; Gn—galena; Qtz—quartz; Ser—sericite; Cal—calcite; Chl—chlorite.



**Figure 4.** Photomicrographs (a–f) and BSE images (g–i) of different mineralization stages from the Fang'an gold deposit: (a) euhedral-to-subhedral pyrite grains; (b) reflected light photograph showing pyrite grains occur in quartz–sericite stage; (c) chalcopyrite and galena hosted in coarse pyrite grains (Py2); (d,e) paragenesis of pyrite, chalcopyrite, sphalerite, and galena in polymetallic sulfide stage; (f) reflected light photograph showing intruding calcite veins from stage II; (g) Py1 has relatively clean surface; (h,i) mineral inclusions and voids in Py2 and Py3. Ccp—chalcopyrite; Py—pyrite; Sp—sphalerite; Gn—galena; Qtz—quartz; Ser—sericite; Cal—calcite; Ele—electrum.

A combination of drill core observation and microscopic analysis was used to determine mineral assemblages, structures, texture, and crosscutting relationships between ore veins. The detailed paragenesis was described by Wang et al. (2022) [16]. Four stages of mineralization were noted in the Fang'an deposit (Figure 5), including the quartz–sericite stage (I), which is defined by sericite–quartz altered rocks, or pyrite–milky white quartz veins in places (Figure 3a,b). Small amounts of euhedral-to-subhedral pyrite (Py1) grains are developed (Figure 4a) and they have relatively clean surfaces (Figure 4g). In the quartz–pyrite stage (II), quartz veins containing pyrite are identified. Pyrite (Py2) occurs as coarse euhedral cubes and subhedral aggregates (Figure 3c,d). Chalcopyrite and galena generally present as irregular inclusions, or are hosted in open fractures in pyrite (Figure 4c,h). In the polymetallic sulfide stage (III), the mineral assemblage is quartz, pyrite, galena, chalcopyrite, and sphalerite. Quartz is usually dark gray (Figure 3e). Pyrite (Py3) occurs as fine-grained subhedral and anhedral aggregates (Figure 4d,e,i). In the carbonate stage (IV), the mineral assemblage is calcite, quartz, and sericite and forms veinlet structures that cut through the earlier stages (Figures 3f and 4f).

| Stage<br>Mineral | Quartz-sericite stage                                                                | Quartz-pyrite stage                                                                  | Polymetallic sulfide stage                                                            | Carbonate stage                                                                       |
|------------------|--------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| Pyrite           |    |                                                                                      |                                                                                       |                                                                                       |
| Chalcopyrite     |                                                                                      |    |                                                                                       |                                                                                       |
| Sphalerite       |                                                                                      |  |                                                                                       |                                                                                       |
| Galena           |                                                                                      |  |                                                                                       |                                                                                       |
| Quartz           |  |                                                                                      |                                                                                       |                                                                                       |
| Sericite         |   |                                                                                      |                                                                                       |  |
| Calcite          |                                                                                      |                                                                                      |  |                                                                                       |
| Gold             |                                                                                      |  |                                                                                       |                                                                                       |

**Figure 5.** Mineral paragenetic sequence of the Fang'an gold deposit.

### 3. Sample Description and Analytical Methods

#### 3.1. Sampling and Petrographic Observations

In this study, 15 samples were collected from drill cores (ZK141 and ZK1665) and prepared as polished into sections for petrographic study. The quartz–pyrite stage ore samples, in which pyrites were coeval with galena, were selected from drill cores (ZK141) for Pb–Rb–Sr isotopic analyses. Four samples of different stages were selected from drill cores (ZK141 and ZK1665) for in situ sulfur isotope analyses. From these, single mineral selections were performed at Hebei ChengPu Testing Technology Co. (Langfang, China). The samples were washed, dried, crushed, and sieved to select single mineral samples of pyrite and galena with a purity of over 99% using binoculars. The Pb–Rb–Sr isotope testing on the samples was completed in an analytical laboratory at Beijing Research Institute of Uranium Geology (BRIUG), China. In situ sulfur isotope testing analysis of thin sections of different stages of pyrite was carried out using LA–MC–ICP–MS at the Institute of Geology, Chinese Academy of Geological Sciences (CAGS).

#### 3.2. Rb–Sr Isotope

For the Rb–Sr isotope analyses, the selected pyrite grains were ground into powdery form, then ultrasonically cleaned for 30 min with Milli-Q water. After the drying process at a low temperature, pyrites samples (each weighing 200 mg) were completely dissolved

in mixed acid, which consists of 1 mL HCl and 3 mL HNO<sub>3</sub> at 120 °C on an electric hot plate. Subsequently, the sample was mixed with hydrochloric acid after being dried with distillation, and the centrifugal separation of Rb, Sr, and other elements was performed with an ion-exchange column from the liquid supernatant. A Phoenix thermal surface ionization mass spectrometer was used for the determination of the Rb and Sr concentrations of the samples and their isotopic ratios. Analyses of the NBS987 standard yielded a mean <sup>87</sup>Sr/<sup>86</sup>Sr ratio of  $0.710233 \pm 6$  (2 $\sigma$ ). The total procedure blank for Rb and Sr analyses was  $3 \times 10^{-9}$  g. The accuracy of the Rb/Sr ratio and Sr concentration were 1% and  $10^{-5}$ , respectively. More details about the analysis can be found in Li et al. (2008) and Yang et al. (2010) [22,23]. Mass spectrometry was performed using a Phoenix thermal surface ionization mass spectrometer [24], and regression analysis for the age calculation was performed using ISOPLOT 3.0 [25].

### 3.3. In-Situ Sulfur Isotope

In situ sulfur isotope analyses were carried out using LA-MC-ICP-MS, following the methods of Li et al. (2019) [26]. An MC-ICP-MS (Neptune Plus) equipped with a laser ablation system (Resolution S155) was used for the analyses. Helium was used as the carrier gas for the ablation cell in the laser ablation system. For single-spot analysis, the laser diameter was 32  $\mu$ m with a laser repetition rate of 6 Hz. The energy fluency of the laser was approximately 5 J/cm<sup>2</sup>. The Neptune Plus instrument was outfitted with nine Faraday cups (FCs) fitted with  $10^{11}$   $\Omega$  resistors. To reduce polyatomic interferences, all measurements were performed at medium resolution with a revolving power that was always greater than 7000. The FCs (L3, C, and H3) concurrently and statically collected signals for <sup>32</sup>S, <sup>33</sup>S, and <sup>34</sup>S. Sulfur isotope mass fractionation was corrected using the standard-sample bracketing method (SSB). The analysis used certified international standards (including Pyrite of Balmat) and working reference samples (pyrite YP-136), with the reference standard values of  $\delta^{34}\text{S}_{\text{V-CDT}}$  reported by Crowe and Vaughan (1996) and Li et al. (2019) [26,27]. The analytical precision calculated from the replicate analyses of the samples was better than 0.5 per mil.

### 3.4. Lead Isotope

An ISOPROBE-T thermal surface ionization mass spectrometer was adopted for the analysis of the Pb isotopes. About 200 mg pyrite or 3 mg galena powder was transferred into a low-pressure digestion tank (PFA) and a mixture of HF-HNO<sub>3</sub>-HClO<sub>4</sub> was added for 24 h. Subsequently, the solution was evaporated to dryness and then dissolved by adding HCl (6 mol/L) to transform the Pb into Pb-chloride and evaporated to dryness again. Then, Pb was separated and purified in a Bio-Rad AG-1  $\times$  8 anion exchange resin column using HBr solution (0.5 mol/L). A total of 1 mL HCl (6 mol/L) was used to resolve the Pb in a Teflon beaker followed by distilling to dryness; the mixture was then coated on a Re filament using the H<sub>3</sub>PO<sub>4</sub> and silicon gel method for analysis using an ISOPROBE-T thermal surface ionization mass spectrometer. The measured Pb isotopes were calibrated for instrument mass fractionation by reference to replicate analyses of the standard NBS 981. The determined <sup>208</sup>Pb/<sup>206</sup>Pb, <sup>207</sup>Pb/<sup>206</sup>Pb, and <sup>204</sup>Pb/<sup>206</sup>Pb ratios for NBS 981 were  $2.164940 \pm 0.000015$ ,  $0.914338 \pm 0.000007$ , and  $0.0591107 \pm 0.0000002$ , respectively. The total blank for Pb was <100 pg. The measurement procedures and reference materials were described in detail by Wang et al. (2017) [28].

## 4. Results

### 4.1. Rb and Sr Isotope Analysis

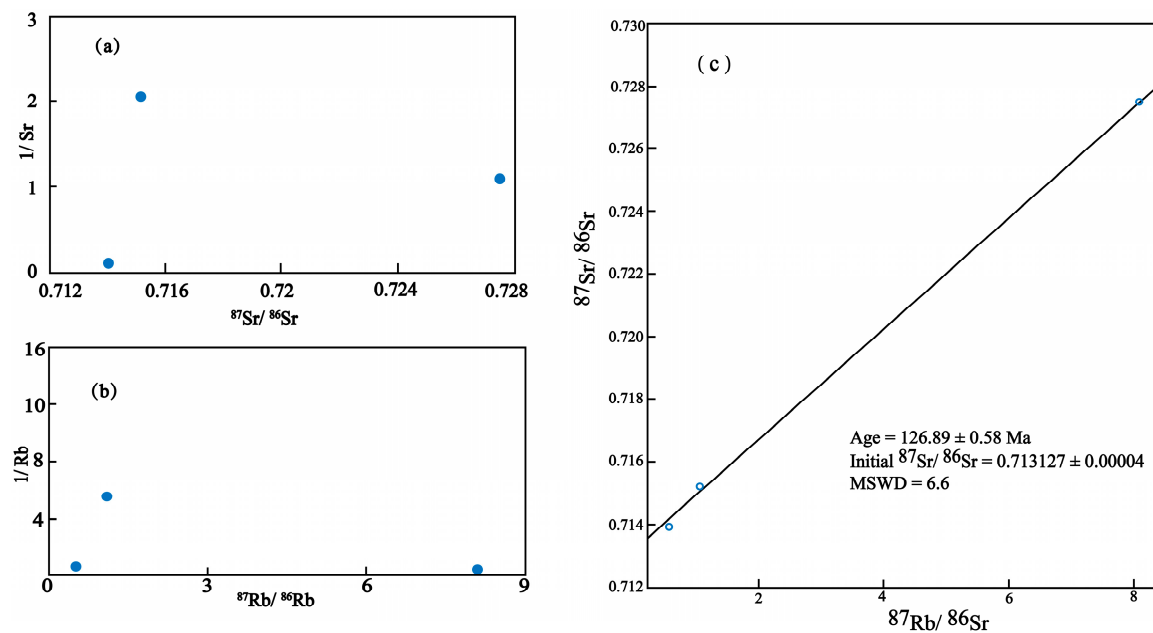
A total of three Rb-Sr isotope samples were selected from the Fang'an deposit, composed of pyrites in the quartz-pyrite stage. The Rb-Sr isotope analytical results for the pyrite samples are listed in Table 1. The Rb and Sr contents in the samples were 0.182–2.53 ppm and 0.482–9.46 ppm, respectively, with <sup>87</sup>Rb/<sup>86</sup>Sr ratios of 0.5361–8.0946 and <sup>87</sup>Rb/<sup>86</sup>Sr analytical uncertainty (2 $\sigma$ ) values of 0.714043–0.727487, indicating that the



range of  $^{87}\text{Rb}/^{86}\text{Sr}$  ratios is relatively large, while the distribution of the analytical uncertainty is relatively concentrated. ISOPLOT 3.0 software was adopted to analyze the test results [25], with a  $2\sigma$  index for the dating error. The value of  $^{87}\text{Rb}/^{86}\text{Sr}$  yielded an Rb–Sr isochron age of  $126.89 \pm 0.58$  Ma (MSWD = 6.6) (Figure 6c), with an initial  $^{87}\text{Sr}/^{86}\text{Sr}$  value of  $0.713127 \pm 0.00004$ .

**Table 1.** The Rb/Sr isotope contents and ratios of pyrite in the Fang’an gold deposit.

| Sample    | Rb ( $\times 10^{-6}$ ) | Sr ( $\times 10^{-6}$ ) | $^{87}\text{Rb}/^{86}\text{Sr}$ | $^{87}\text{Sr}/^{86}\text{Sr}$ | Std Err  |
|-----------|-------------------------|-------------------------|---------------------------------|---------------------------------|----------|
| ZK141–H8  | 0.182                   | 0.482                   | 1.0941                          | 0.715128                        | 0.000029 |
| ZK141–H11 | 2.53                    | 0.905                   | 8.0946                          | 0.727487                        | 0.000024 |
| ZK141–N2  | 1.75                    | 9.46                    | 0.5361                          | 0.714043                        | 0.000023 |



**Figure 6.** (a,b).  $^{87}\text{Sr}/^{86}\text{Sr}$ – $\text{Sr}^{-1}$ ,  $^{87}\text{Rb}/^{86}\text{Sr}$ – $\text{Rb}^{-1}$  diagrams of pyrite; (c). Rb–Sr isochron of pyrite inclusion ages from Fang’an gold deposits.

#### 4.2. In Situ Sulfur Isotope of Pyrite

The  $\delta^{34}\text{S}$  values of hydrothermal pyrite from the Fang’an deposit have a narrow range of 3.73‰~6.81‰ ( $n = 25$ ). The isotopic data ( $n = 25$ ) for in situ pyrite isotope analyzed ( $\delta^{34}\text{S}$ ) using LA–MC–ICP–MS are provided in Table 2, as shown in Figure 7. The  $\delta^{34}\text{S}$  values of Py1 range between 3.73‰ and 4.95‰ with an average of 4.45‰ ( $n = 5$ ). The  $\delta^{34}\text{S}$  values of Py2 range between 4.55‰ and 6.81‰ with an average of 5.51‰ ( $n = 10$ ). The  $\delta^{34}\text{S}$  values of Py3 range between 4.09‰ and 5.9‰ with an average of 5.18‰ ( $n = 10$ ).

**Table 2.** The sulfur isotopic composition of pyrite from the Fang’an deposit and related.

| Site    | Sample No.  | Testing Object | $\delta^{34}\text{S}_{\text{V-CDT}}/\text{‰}$ | References |
|---------|-------------|----------------|-----------------------------------------------|------------|
| Fang’an | ZK141–H11–1 | Py1            | 3.73                                          | This study |
|         | ZK141–H11–2 |                | 4.95                                          |            |
|         | ZK141–H11–3 |                | 4.81                                          |            |
|         | ZK141–H11–4 |                | 3.84                                          |            |
|         | ZK141–H11–5 |                | 4.93                                          |            |



Table 2. Cont.

| Site    | Sample No.    | Testing Object    | $\delta^{34}\text{Sv-CDT}/\text{‰}$ | References                 |
|---------|---------------|-------------------|-------------------------------------|----------------------------|
| Fang'an | ZK141-K3-1-1  | Py2               | 5.86                                | This study                 |
|         | ZK141-K3-1-2  |                   | 6.81                                |                            |
|         | ZK141-K3-1-3  |                   | 6.09                                |                            |
|         | ZK141-K3-1-4  |                   | 5.69                                |                            |
|         | ZK141-K3-1-5  |                   | 6.12                                |                            |
|         | ZK1665-F4-2-2 |                   | 5.31                                |                            |
|         | ZK1665-F4-2-3 |                   | 4.55                                |                            |
|         | ZK1665-F4-2-4 |                   | 4.69                                |                            |
|         | ZK1665-F4-2-5 | Py3               | 4.84                                |                            |
|         | ZK1665-F4-2-6 |                   | 5.11                                |                            |
|         | ZK1665-F4-1-4 |                   | 4.78                                |                            |
|         | ZK1665-F4-1-5 |                   | 4.49                                |                            |
|         | ZK1665-F4-1-3 |                   | 4.09                                |                            |
|         | ZK1665-F4-1-6 |                   | 4.5                                 |                            |
|         | ZK141-H1-1    |                   | 5.66                                |                            |
|         | ZK141-H1-2    |                   | 5.53                                |                            |
|         | ZK141-H1-3    |                   | 5.66                                |                            |
|         | ZK141-H1-4    |                   | 5.49                                |                            |
|         | ZK141-H1-5    |                   | 5.9                                 |                            |
|         | ZK141-H1-6    |                   | 5.7                                 |                            |
| Rongdu  |               | Galena            | 2.3                                 | Wei (2011)<br>[14]         |
|         |               | Pyrite            | 2.5                                 |                            |
|         |               | Galena            | 6.8                                 |                            |
|         |               |                   | 3.1                                 | Zong et al. (2022)<br>[29] |
|         | DQT-Py-1      | Pyrite            | 6.8                                 |                            |
|         | DQT-Py-2      |                   | 5.8                                 |                            |
| Hekou   | DQT-Gn-1      | Galena            | 3.7                                 |                            |
|         | DQT-Gn-2      |                   | 1.3                                 |                            |
|         | 1             | Barren Pyrite     | 6.47                                | Liu et al. (2023)<br>[30]  |
|         | 2             |                   | 6.33                                |                            |
|         | 3             |                   | 6.29                                |                            |
|         | 4             |                   | 6.37                                |                            |
|         | 5             |                   | 6.12                                |                            |
|         | 6             |                   | 6.24                                |                            |
|         | 7             |                   | 6.07                                |                            |
|         | 8             |                   | 6.02                                |                            |
|         | 9             |                   | 5.98                                |                            |
|         | 10            |                   | 6                                   |                            |
|         | 11            |                   | 6.2                                 |                            |
|         | 12            |                   | 6.19                                |                            |
|         | 13            |                   | 6.47                                |                            |
|         | 14            |                   | 6.58                                |                            |
|         | 15            |                   | 6.51                                |                            |
|         | 16            |                   | 6.73                                |                            |
|         | 1             | Auriferous Pyrite | 6.08                                |                            |
|         | 2             |                   | 6.1                                 |                            |
|         | 3             |                   | 5.81                                |                            |
|         | 4             |                   | 5.77                                |                            |
|         | 5             |                   | 5.83                                |                            |
|         | 6             |                   | 6.17                                |                            |
|         | 7             |                   | 5.74                                |                            |
|         | 8             |                   | 5.73                                |                            |
|         | 9             |                   | 5.65                                |                            |
|         | 10            |                   | 5.74                                |                            |
|         | 11            |                   | 5.97                                |                            |
|         | 12            |                   | 6.08                                |                            |
|         | 13            |                   | 6.4                                 |                            |
|         | 14            |                   | 6.18                                |                            |

Table 2. Cont.

| Site    | Sample No. | Testing Object | $\delta^{34}\text{Sv-CDT}/\%$ | References          |
|---------|------------|----------------|-------------------------------|---------------------|
| Dykes   | 2011–47    | Lamprophyre    | 2.1                           | Yang (2020)<br>[9]  |
|         | 2011–50    |                | 1.1                           |                     |
| Xigudui | RD–10      | Plagiogneiss   | 4.1                           |                     |
|         | DGS–17     |                | 4                             |                     |
|         | 2207–5     |                | 4.4                           |                     |
|         | 2011–18    | Amphibolite    | 2                             |                     |
|         |            | Pyrite         | 4.22                          | Chen (2021)<br>[31] |
|         |            |                | 4.77                          |                     |
|         |            |                | 4.33                          |                     |
|         |            |                | 5.63                          |                     |
|         |            |                | 4.65                          |                     |

#### 4.3. Lead Isotopic Composition of Sulfide

The lead isotopic compositions of galena and pyrite from the Fang'an gold deposit are relatively uniform, as shown in Table 3 and illustrated in Figures 8 and 9. The values of  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$  of galena and pyrite, together with the  $^{206}\text{Pb}/^{207}\text{Pb}$  values of galena and pyrite, are shown in Table 3, with  $^{206}\text{Pb}/^{204}\text{Pb}$  values of 16.759~16.93,  $^{207}\text{Pb}/^{204}\text{Pb}$  values of 15.311~15.402,  $^{208}\text{Pb}/^{204}\text{Pb}$  values of 37.158~37.548, and  $^{206}\text{Pb}/^{207}\text{Pb}$  values of 1.0917~1.2022. The values of  $\mu$ ,  $\omega$ , and Th/U were determined using the single-stage Pb evolution model calculation. The average values for these parameters were 9.24, 39.18, and 4.1, respectively (Table 3). Table 3 also lists the calculated  $\Delta\beta$  and  $\Delta\gamma$  values, including data from previous studies.

Table 3. Lead isotopic compositions of pyrite and galena from the Fang'an gold deposit and related.

| Sample    | Test Object | Pb Isotopic Ratios                |                                   |                                   |                                   | Parameters |          |      |               |                | References                           |
|-----------|-------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|------------|----------|------|---------------|----------------|--------------------------------------|
|           |             | $^{208}\text{Pb}/^{204}\text{Pb}$ | $^{207}\text{Pb}/^{204}\text{Pb}$ | $^{206}\text{Pb}/^{204}\text{Pb}$ | $^{206}\text{Pb}/^{207}\text{Pb}$ | $\mu$      | $\omega$ | Th/U | $\Delta\beta$ | $\Delta\gamma$ |                                      |
| ZK141–H1  | Galena      | 37.158                            | 15.331                            | 16.759                            | 1.0931                            | 9.18       | 38.29    | 4.04 | 0.07          | −6.47          | This study                           |
| ZK141–H13 |             | 37.453                            | 15.372                            | 16.924                            | 1.101                             | 9.23       | 39.02    | 4.09 | 2.74          | 1.42           |                                      |
| ZK141–H8  | Pyrite      | 37.47                             | 15.397                            | 16.881                            | 1.0964                            | 9.29       | 39.67    | 4.13 | 4.37          | 1.87           |                                      |
| ZK141–H6  |             | 37.548                            | 15.402                            | 16.93                             | 1.0992                            | 9.29       | 39.76    | 4.14 | 4.7           | 3.96           |                                      |
| BB9–1     | Feldspar    | 38.4123                           | 15.5937                           | 17.9498                           | 1.1511                            |            |          |      | 17.2          | 27.07          | Yang et al.,<br>(2019) [32]          |
| BB9–2     |             | 38.3915                           | 15.5896                           | 17.9098                           | 1.1488                            |            |          |      | 16.93         | 26.51          |                                      |
| BB9–3     |             | 38.3976                           | 15.5919                           | 17.9175                           | 1.1492                            |            |          |      | 17.08         | 26.67          | Wang et al.,<br>(2012) [6]           |
|           |             | 36.869                            | 15.376                            | 17.03                             | 1.1076                            |            |          |      | 3             | −14.2          |                                      |
|           |             | 37.492                            | 15.397                            | 17.186                            | 1.1162                            |            |          |      | 4.37          | 2.46           |                                      |
|           | Whole rock  | 34.54                             | 15.659                            | 18.826                            | 1.2022                            |            |          |      | 21.46         | −76.47         | Sang et al.,<br>(1990) [33]          |
|           |             | 37.23                             | 15.38                             | 16.79                             | 1.0917                            |            |          |      | 3.26          | −4.55          |                                      |
|           |             | 37.7472                           | 15.5027                           | 17.2879                           | 1.1152                            |            |          |      | 11.27         | 9.28           | Dong et al.,<br>(1995) [34]          |
|           |             | 38.1016                           | 15.5563                           | 17.4453                           | 1.1214                            |            |          |      | 14.76         | 18.76          |                                      |
|           |             | 37.6212                           | 15.4679                           | 17.1807                           | 1.1107                            |            |          |      | 9             | 5.91           |                                      |
|           |             | 38.5558                           | 15.4608                           | 17.3121                           | 1.1197                            |            |          |      | 8.53          | 30.9           |                                      |
|           |             | 37.8292                           | 15.5158                           | 17.4061                           | 1.1218                            |            |          |      | 12.12         | 11.48          | Tu et al.,<br>(1992,1993)<br>[35,36] |
|           |             | 37.69                             | 15.345                            | 16.946                            | 1.1043                            |            |          |      | 0.98          | 7.75           |                                      |
|           |             | 37.692                            | 15.431                            | 17.134                            | 1.1104                            |            |          |      | 6.59          | 7.81           |                                      |
|           |             | 37.692                            | 15.384                            | 17.273                            | 1.1228                            |            |          |      | 3.52          | 7.81           |                                      |

Abbreviations are as follows:  $\mu$  = initial  $^{238}\text{U}/^{204}\text{Pb}$  ratio;  $\omega$  = initial  $^{232}\text{Th}/^{204}\text{Pb}$  ratio.  $\Delta\beta = (^{207}\text{Pb}/^{204}\text{Pb}/15.33 - 1) \times 1000$ ;  $\Delta\gamma = (^{208}\text{Pb}/^{204}\text{Pb}/37.4 - 1) \times 1000$ . All parameters and Th/U values were determined using Geokit [37,38].

## 5. Discussion

### 5.1. Timing of Gold Mineralization

Two main methods are used to determine the mineralization age of hydrothermal deposits. One method involves the ages of wall rocks (strata or intrusions) to constrain the mineralization age. Another method is directly measuring the ages of ore minerals or altered minerals [39]. After the first attempt at geochronological Rb–Sr dating of sulfide minerals was made by Nakai et al. (1990) [40], many studies have been conducted in this regard, proving the effectiveness of using Rb–Sr methods for dating hydrothermal

deposits [41,42]. This suggests that Rb–Sr isotope pyrite dating is an effective and direct method for defining the formation ages of hydrothermal sulfide deposits.

As proposed by previous studies on the binary mixed system of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, a set of samples participating in the isochron fit by their  $^{87}\text{Sr}/^{86}\text{Sr}\text{--Sr}^{-1}$  and  $^{87}\text{Rb}/^{86}\text{Sr}\text{--Rb}^{-1}$  values were plotted to determine whether they were mixed lines. When the samples were positively correlated, they were considered to be mixed lines; otherwise, the obtained isochronous ages were considered to be representative of the age of mineralization during the corresponding phase [43]. When the  $^{87}\text{Sr}/^{86}\text{Sr}\text{--Sr}^{-1}$  and  $^{87}\text{Rb}/^{86}\text{Sr}\text{--Rb}^{-1}$  values of the rubidium–strontium isotopes of the Fang'an gold deposit were plotted (Figure 6a,b), it was found that there was no correlation between the elements in the Fang'an gold deposit. The isochronous age obtained via calculations based on the three samples through ISOPLOT software was  $126.89 \pm 0.58$  Ma (MSWD = 6.6) (Figure 6c), and the initial value of  $^{87}\text{Sr}/^{86}\text{Sr}$  was  $0.713127 \pm 0.00004$  with an MSWD value of 6.6. Then, the data were plotted using ISOPLOT software, and we found that the  $^{87}\text{Sr}$  and  $^{87}\text{Rb}$  values did not co-vary with  $^{86}\text{Sr}\text{--Sr}^{-1}$  and  $^{86}\text{Sr}\text{--Rb}^{-1}$ , irrespective of samples (Figure 6a,b), indicating that the age was isochronal and therefore able to reflect the metallogenic age of gold mineralization. The Rb–Sr isotopic age of  $126.89 \pm 0.58$  Ma for pyrite samples was considered to be reliable.

Previous work on the mineralization age of the gold deposits in the Wuhe area utilized various radioisotope dating methods, such as Rb–Sr, Re–Os, K–Ar, and Ar–Ar ore and/or gangue minerals, resulting in distinct isotope ages of 113–134 Ma [4,5,7,9,44]. Furthermore, the Wuhe magmatic rocks are composed of a large number of intermediate–felsic intrusions (115–130 Ma) and a few mafic dikes (116–130 Ma) [44]. Due to their close spatial and temporal relationship, the gold mineralization in the Wuhe area is associated with Early Cretaceous (115–130 Ma) magmatism.

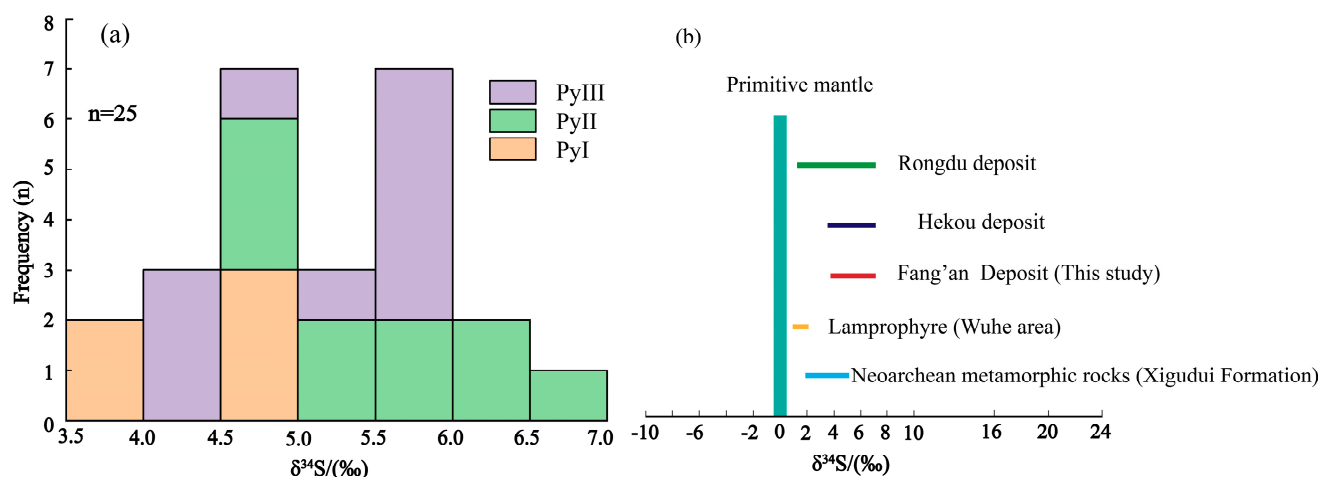
Therefore, we conclude that the Rb–Sr isochron ages of pyrite ( $126.89 \pm 0.58$  Ma) constrain the mineralization age of the Fang'an deposit, coeval with emplacement ages of Early Cretaceous intrusions in the Wuhe area, indicating a genetic link between them.

### 5.2. Ore-Forming Material Source

Sulfur is one of the key elements in gold deposits. Consensus among studies suggests that gold was transported in ore-forming fluids, primarily as bisulfide complexes, and co-precipitated with sulfides, particularly pyrite [45,46]. Consequently, understanding the sulfur isotopic composition of pyrite is crucial for enhancing our knowledge of the sources of ore-forming materials and deposits [47–49].

The  $\delta^{34}\text{S}$  values of hydrothermal pyrite in the three stages of the Fang'an deposit have a narrow range from 3.73‰ to 6.81‰ (Figure 7). There is no obvious difference in the  $\delta^{34}\text{S}$  values of each stage (average 4.45‰–5.51‰–5.18‰) (Figure 7a), indicating that they came from the same source. In addition, the  $\delta^{34}\text{S}$  values of the whole rock and sulfides ( $\delta^{34}\text{S} = 2\text{‰}\sim 5.63\text{‰}$ ) from the Neoproterozoic Xigudui Formation, and lamprophyre ( $\delta^{34}\text{S} = 1.1\text{‰}\sim 2.1\text{‰}$ ) from the Mesozoic intermediate–basic dikes (Figure 7b), have been previously documented. Furthermore, the  $\delta^{34}\text{S}$  values fall within the narrow ranges of these rocks. It is still difficult to establish whether the sources of ore-forming sulfur were magmatic, metamorphic, or mantle.

Although the average  $\delta^{34}\text{S}$  values in Fang'an are close to the value for the Xigudui Formation ( $\delta^{34}\text{S} = 2\text{‰}\sim 5.63\text{‰}$ ), the source of ore-forming sulfur cannot be attributed to the metamorphic rocks of the Neoproterozoic Xigudui Formation, because the gold event occurred about 2 billion years later than the regional high-grade metamorphism. Consequently, these essential components would have been lost from the rocks during this extended period. Furthermore, the age of the gold mineralization (126.89 Ma) is nearly 4 Ma younger than the ages of the regional Mesozoic granites, such as the Nvshan (130 Ma) granitoids [20], thus raising the possibility of magmatic sources of ore-forming fluids.



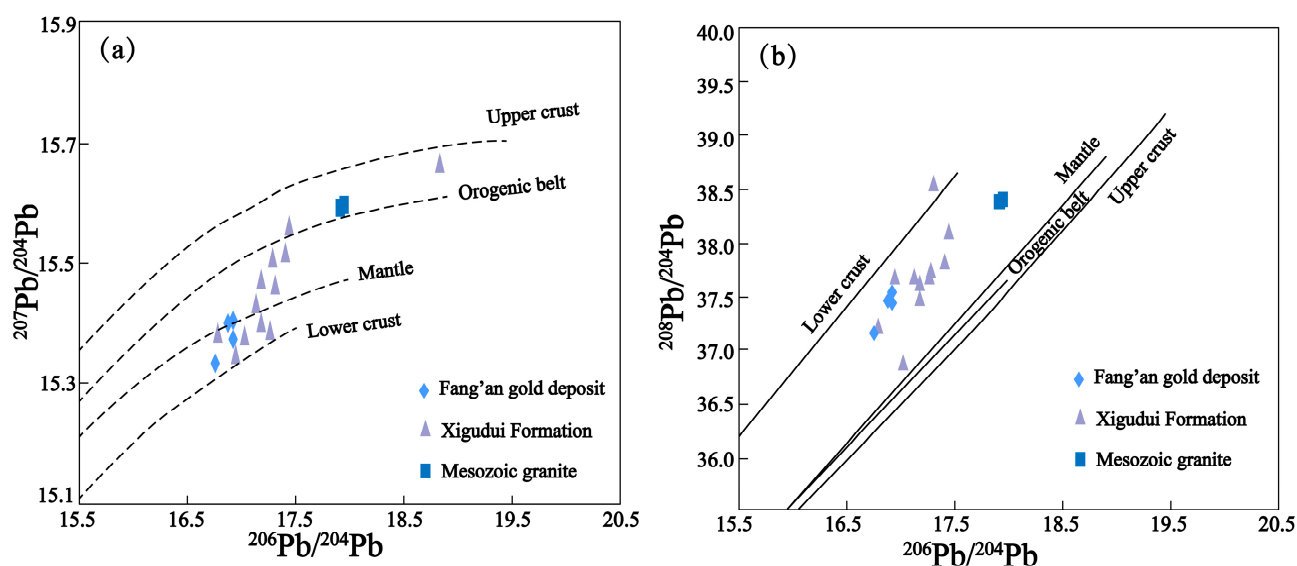
**Figure 7.** (a). Histograms of  $\delta^{34}\text{S}$  values of hydrothermal pyrites from the Fang'an deposit; (b). Natural sulfur isotope reservoirs (modified after [50]) and sulfur isotope composition of sulfide from deposits in the Wuhe area. The Fang'an gold deposit data are from this study; the data of other gold deposits in the Wuhe area are from Table 2.

However, our results show that the  $\delta^{34}\text{S}$  values of these geologic units are comparable; in particular, the  $\delta^{34}\text{S}$  (1.1‰~2.1‰) values of Mesozoic mantle-derived basic–intermediate dikes deviate from the mantle values ( $\delta^{34}\text{S} = \sim 0$ ‰). Mao et al. (2008) proposed that the similar sulfur isotopic compositions of the Mesozoic rocks imply the homogenization of the sulfur isotopic system through crust–mantle interactions [51]. Furthermore, Zhu et al. (2015), using He–Ar isotopes, proposed that during the westward subduction of the paleo-Pacific plate in the Early Cretaceous, parts of the subducted slab remained stagnant in the mantle transition zone under the eastern NCC [52]. In other words, during the Mesozoic mineralization events, it is implied that the ore-forming fluids sourced from a common reservoir were likely associated with processes of magmatic crust–mantle interactions.

In this study, our lead isotope results also confirm that the ore-forming fluids were derived from crust–mantle magmatic activity. Lead isotope compositions (particularly those of sulfide minerals, such as pyrite and galena) are an excellent proxy for constraining the sources of lead in ore-forming fluids [53,54]. Lead isotopes can fingerprint metal sources, reveal the nature of Pb reservoirs, and determine rough tectonic settings for ore formation [55,56].

The Pb isotopic compositions of sulfide minerals in the Fang'an deposit, despite their slight variations (Figure 8), define a linear array in the  $^{207}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  vs.  $^{206}\text{Pb}/^{204}\text{Pb}$  diagrams. The samples from the Fang'an deposit are plotted near or below the average lower crust line in Figure 8a, and between the mantle and lower crust lines in Figure 8b. They were plotted close to the Xigudui Formation, relatively distant from the Mesozoic granites, indicating that the Xigudui Formation was the source of lead for the Late Mesozoic ores of the deposit.

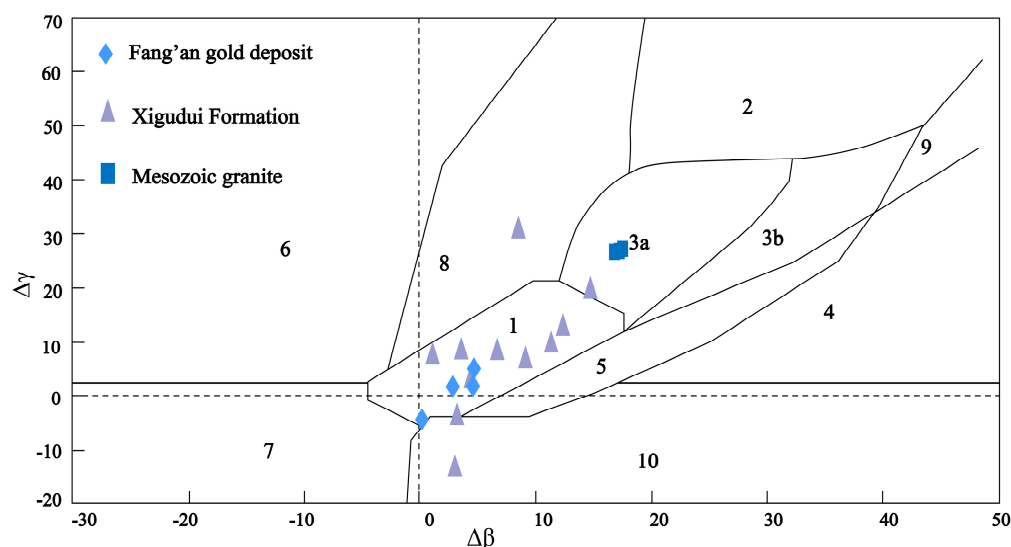




**Figure 8.** Lead isotopic tectonic model for the Fang'an gold deposit, (a,b)  $^{206}\text{Pb}/^{204}\text{Pb}$  vs.  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$  vs.  $^{208}\text{Pb}/^{204}\text{Pb}$  diagrams showing the comparison of the Pb isotope of the Fang'an gold deposit and regional rocks in the Wuhe area and general earth Pb reservoirs (after Zartman and Doe, 1981) [57]. Literature for the Pb isotope data of the regional metamorphic and granite rocks are listed in Table 3.

The samples from the Fang'an gold deposit yielded  $^{206}\text{Pb}/^{207}\text{Pb}$  values of 1.0931–1.101, with an average  $^{206}\text{Pb}/^{207}\text{Pb}$  value of 1.097 (Table 3), which is similar to that of the Xigudui Formation (1.12) but contrasting with that of the Mesozoic granites (1.149). This indicates that the ore-forming lead was mainly sourced from common lead ( $^{206}\text{Pb}/^{207}\text{Pb} = 0.89\text{--}1.20$ ) [58,59] rather than radiogenic lead. The growth in radiogenic Pb resulting from the decay of U and Th after the formation of these sulfides was negligible. The lead isotopic coefficients (U, Th, and Pb) were different in the upper crust, lower crust, and mantle. Therefore, the source of Pb can also be determined using Pb isotope parameters, such as the  $\mu$  ( $^{238}\text{U}/^{204}\text{Pb}$ ),  $\omega$  ( $^{232}\text{Th}/^{204}\text{Pb}$ ), and  $\kappa$  (Th/U) values [60–64]. The  $\mu$  values of the Fang'an sulfides (9.18–9.29, average of 9.24) are slightly higher than the average for the mantle (8.92) [61–65]. In contrast, the  $\omega$  values of the Fang'an sulfides (38.29–39.76, average of 39.18) are distinctly higher than the average for the crust (36.84) [62]. Low  $\mu$  and high  $\omega$  values are characteristic of the lower crust [60–64]. Moreover, the  $\kappa$  values of the Fang'an sulfides (4.04–4.14, average of 4.1) are also highly similar to the average for the crust (4) [66,67]. This further supports the assertion that magmatic crust–mantle sources played an important role in Fang'an ore formation. In Figure 9, the samples from the Xigudui Formation are chiefly plotted in the mantle domains (labelled 1 in Figure 9), with a few in the magmatic crust–mantle mixture in a subduction setting, i.e., the magmatic arc (labeled 3a in Figure 9). This is consistent with the previous understanding that crust–mantle magmatism resulted in the formation of the granites, followed by gold mineralization.

In summary, due to the degassing of mantle-derived magmas in the shallow parts of the crust, it can be determined that the source of ore-forming sulfur and lead was crust–mantle magmatic activity in the Wuhe area.



**Figure 9.** The  $\Delta\beta - \Delta\gamma$  tectonic discrimination (after Zhu, 1998) [68]. Notation of fields: 1, mantle; 2, upper crust; 3, subduction setting mixed by upper crust and mantle (3a = magmatism, 3b = sedimentation); 4, chemical sediment; 5, seafloor hydrothermal systems; 6, middle- to high-grade metamorphism; 7, high-grade metamorphosed lower crust; 8, orogenic belts; 9, old shales in upper crust; 10, retrograde metamorphism.

### 5.3. Ore Genesis

In the Early Cretaceous period, the westward subduction of the paleo-Pacific plate caused parts of the subducted slab to remain stagnant in the mantle transition zone under the eastern NCC [69–71]. This led to the intense metasomatism of the lithospheric mantle and extensive crust–mantle magmatism in the Wuhe area, increasing oxygen fugacity ( $f_{O_2}$ ) and leading to the enrichment of  $^{34}\text{S}$  [52,72]. The  $\delta^{34}\text{S}$  values of early Py1 (average 4.45‰) are obviously higher than that of the primitive mantle ( $\delta^{34}\text{S} = \sim 0\text{‰}$ ) and contemporaneous mantle-derived lamprophyre ( $\delta^{34}\text{S} = 1.1\text{‰} \sim 2.1\text{‰}$ ). This indicates the presence of a more  $^{34}\text{S}$ -rich source, which is related to the degassing and intense metasomatism of the lithospheric mantle [49,73]. And this change can be seen in the in situ S isotope analysis on pyrite from different stages (Figure 7a), revealing an increase in  $\delta^{34}\text{S}$  values from Py 1 (average 4.45‰) to Py 2 (average 5.51‰). When ore-forming fluids transformed to stage II, the magmatic fluids mixed with meteoric waters characterized by higher  $f_{O_2}$  and lower temperatures, resulting in decreasing temperature and increasing  $f_{O_2}$  of the ore-forming fluids [49,74]. Recently, O and C–O isotope data have confirmed that the initially magmatic ore-forming fluids were subsequently mixed with meteoric water [15]. Meanwhile, the Rb–Sr isochron dating results ( $126.89 \pm 0.58$  Ma) are consistent with Early Cretaceous (115–130 Ma) magmatism in the Wuhe area [44]. This age coincidence allows us to propose that the sources of the ore-forming fluids were closely related to crust–mantle magmatism. Notably, the decline in  $\delta^{34}\text{S}$  values from Py 2 (average 5.51‰) to Py 3 (average 5.18‰) was related to fluid immiscibility [75,76]. The study by Liu (2023) on the Hekou deposit finds that the coexistence of liquid-rich and  $\text{CO}_2$ -rich fluid inclusions in quartz near pyrite provides evidence of fluid immiscibility in  $\text{NaCl-H}_2\text{O-CO}_2$  fluids during the polymetallic sulfide stage [30,75,76]. When fluid immiscibility occurs, pyrite not only captures more precious and base metals, but also exhibits characteristics of sulfide precipitation [77–79]. As shown in Figure 4, the surfaces of pyrite (Py2 and Py3) display abundant sulfide inclusions. When ore-forming fluid transformed to Stage II and Stage III, characterized by temperature decrease, pressure fluctuation, and fluid immiscibility, the  $\text{H}_2\text{S}$  was fractionated strongly into the vapor phase and the activity of  $\text{HS}^-$  lowered. This process might have led to the decomposition of  $\text{Au}(\text{HS})-2$  and enrichment of the gold [74,80,81].

Taken together, we can conclude that the formation of the Fang'an deposit was associated with crust–mantle magmatism in the 115–130 Ma period, and thus, it can be

classified as a magmatic (crust–mantle)–hydrothermal-type deposit formed during the Early Cretaceous. During ca. 130 to 115 Ma, significant lithospheric thinning in the NCC was caused by the subduction of the paleo–Pacific plate. This period of tectonic activity along the TLFZ was marked by asthenospheric underplating and the emplacement of numerous mantle- and crust-related intrusions into the shallow crust. These magmatic fluids migrated upwards along fractures or through highly permeable strata to a lower pressure level. Meanwhile, meteoric water entered the magmatic fluid, leading to fluid mixing, a decrease in temperature and pressure, and the fluid immiscibility within the ore-forming hydrothermal systems, give rise to the precipitation of native Au, and polymetallic sulfides in the Fang’an deposit.

## 6. Conclusions

Based on a study of the geological characteristics of the Fang’an deposit, the S–Pb isotopes of the sulfides, and the Rb–Sr isotopic composition of the pyrite, the following conclusions are drawn:

(1) The S–Pb isotope data indicates that the ore-forming material sources were derived from crust–mantle magmatic activity. Py1 has higher  $\delta^{34}\text{S}$  values, suggesting degassing and intense metasomatism of the lithospheric mantle during the early mineralization stage. Py2 (average 5.51‰) are higher than Py1 (average 4.45‰), indicating that the magmatic fluids mixed with meteoric waters. The  $\delta^{34}\text{S}$  values for Py3 (average 5.18‰) are lower than Py2 (average 5.51‰), revealing that it is related to fluid immiscibility.

(2) The mineralization age of the Fang’an deposit is  $126.89 \pm 0.58$  Ma, closely associated with magmatic activity.

(3) The Fang’an deposit and other deposits in the Wuhe area have similar geochronology, ore-forming source systems, and stable isotope compositions, indicating that they belong to the same magmatic–hydrothermal system.

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**Data Availability Statement:** The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Conflicts of Interest:** The authors declare no conflicts of interest.

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