

Article

Ore Mineralogy, Fluid Inclusion Geochemistry, and Zircon U-Pb Geochronology of the Nanmingshui Gold Deposit in East Junggar, Xinjiang, Northwest China: Implications for Ore Genesis

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Abstract: The Nanmingshui gold deposit, located in the eastern segment of the Kalamaili gold belt (KGB), is hosted by the sub-greenschist facies rocks of the Lower Carboniferous Jiangbasitao Formation. The genesis of this deposit, however, has been debated for decades because of controversial constraints on the *P-T-X* conditions and origins of hydrothermal fluid and mineralization age. In this study, we present gold-bearing sulfide compositions, fluid inclusions, H-O isotopes, and the results of hydrothermal zircon U-Pb dating to provide new insights into the genesis of the gold deposit. Three gold mineralization stages are recognized: quartz–pyrite–minor native gold veins (early), quartz–tourmaline–arsenopyrite–pyrite–gold–polymetallic sulfide veins (middle), and quartz–calcite veinlets (late). Gold predominantly occurs as native gold with high fineness ranging from 941 to 944 in sulfides and quartz, and some as solid solutions (Au⁺) within the lattice of pyrite and arsenopyrite. Three types of primary fluid inclusions are identified in hydrothermal quartz: CO₂–H₂O (C-type), aqueous (W-type), and pure CO₂ (PC-type) inclusions. The early-stage quartz mainly contains C-type and minor W-type inclusions, with total homogenization temperatures (*T_h*) of 220–339 °C, salinities of 0.4–3.7 wt.% NaCl eqv., and bulk densities of 0.66–1.01 g/cm³. All three types of inclusions are observed in the middle-stage quartz, of which the C- and W-type inclusions yield *T_h* values of 190–361 °C, with salinities of 0.4–6.0 wt.% NaCl eqv. and bulk densities of 0.69–0.99 g/cm³. The late-stage quartz contains only W-type inclusions that have lower *T_h* values of 172–287 °C, higher salinities of 1.4–6.9 wt.% NaCl eqv., and bulk densities of 0.79–0.95 g/cm³. Trapping pressures estimated from C-type inclusions in the early and middle stages cluster at 280–340 MPa and 220–310 MPa, respectively, corresponding to metallogenic depths of 10–13 km and 8–11 km. The H-O isotopic compositions ($\delta^{18}\text{O}_{\text{water}} = 1.8\text{--}10.9\text{‰}$, $\delta\text{D} = -99\text{ to }-62.9\text{‰}$) and microthermometric data indicate that the ore-forming fluids belong to medium–high-temperature, low-salinity, medium-density, and CO₂-rich-H₂O-NaCl $\pm$ CH₄ $\pm$ N₂ systems, probably originating from metamorphic water. Fluid immiscibility is a crucial mechanism for gold precipitation. Additionally, the U-Pb dating of hydrothermal zircons, from the auriferous quartz–tourmaline vein, yield a weighted mean ²⁰⁶Pb/²³⁸U age of 314.6 $\pm$ 9.6 Ma. Taking all of the above, the Nanmingshui deposit can be reasonably classed as a typical mesozonal orogenic gold deposit in the KGB, which was formed in a Late Carboniferous tectonic transition from syn-collision between the Jiangjunmiao accretionary complex and Yemaquan arc to post-collision in the East Junggar Orogen. Our results serve to better understand the gold mineralization and genesis of the Late Paleozoic orogenic system in the Kalamaili area, Xinjiang.



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1. Introduction

Orogenic gold deposits, a distinctive class of epigenetic mineral deposits, are currently the major source of global gold production [1,2]. They typically form at a 5 to 18 km depth under greenschist–amphibolite facies conditions, via deformation-induced fluid circulation preferentially driven along ductile–brittle transcurrent structures deeply rooted into the lithosphere at Archean-to-Phanerozoic-convergent tectonic margins [1,3]. Since the term “Orogenic gold deposits” was proposed by Groves et al. [3], numerous world-class and even several giant orogenic gold deposits have been reported worldwide, e.g., the largest Archean Golden Mile and Mt Charlotte gold deposits at Kalgoorlie in the Yilgarn Craton, west Australia [4]; the Obuasi, Damang, and Bogoso–Prestea gold deposits in the Paleoproterozoic Ashanti greenstone belt, southwest Ghana [5,6]; the Gara, Yalea, and Goukoto gold deposits in the world-class Loulo mining district, Mali [7,8]; and the Jiaojia, Sanshandao, and Xincheng gold deposits in the Jiaodong Peninsula, China [9–11]. As one of the principal types of gold deposits in the metamorphic belt, orogenic gold deposits have been relatively well documented in tectonic and geodynamic settings, geology, ore fluids and isotopic chemistry, and genetic models [12–16]. Nevertheless, there remains an ongoing and spirited debate on the fluid sources of orogenic gold deposits, and various models have been proposed, such as the shallow crustal meteoric-fluid [17], magmatic–hydrothermal [18,19], and supracrustal metamorphic models [20]. The latter emphasizes a metamorphic fluid source resulting from the metamorphic devolatilization of supracrustal rocks under greenschist- to amphibolite-facies conditions and is widely accepted [1]. However, significant magmatic fluids are now input to explain the enrichment of tellurides in individual orogenic gold deposits [19,21]. Essentially, the spatiotemporal and genetic associations between gold mineralization and magmatism in an orogeny are still subjects in the study of orogenic gold deposits.

The Central Asian Orogenic Belt (CAOB) or Altaids represents the complex evolution of the Neoproterozoic–Paleozoic orogenic belt, which is situated between the Siberian craton to the north and the Tarim and North China (Sino-Korean) craton to the south (Figure 1A) [22]. Based on metallogenic models applied for either accretionary orogeny or collisional orogeny, the CAOB could contain orogenic deposits formed during the processes of oceanic plate subduction, terrane accretion, and continent–continent collision. Indeed, numerous world-class super-large and large orogenic gold deposits have been discovered in the Southern Tianshan area, the Chinese Tianshan area, Altay, and the West Junggar Orogen, e.g., the Muruntao (5246 t Au), Kumtor (570 t Au), Sawayaerdun (>100 t Au), and Hatu (56 t Au) gold deposits [23–25]. As an important part of the CAOB, however, orogenic deposits are rarely reported in the East Junggar Orogen, North Xinjiang, even though a large number of lode gold deposits and occurrences have been detected and worked by local farmers in the Kalamaili Gold Belt (KGB) in past decades [26]. The majority of these lode deposits, represented by the Shuangquan (24 t Au), Jinshuiquan (10 t Au), Nanmingshui (10 t Au), and Sujiquandong (7 t Au) gold deposits, are confined to a narrow KGB bounded by the NW-NWW-trending Qingshui–Sujiquan and Kalamaili faults (Figure 1C), and are similar to those of Phanerozoic gold deposits in geology and geochemistry [27]. Most studies in this area mainly focused on Paleozoic tectonic evolution, post-collisional magmatism, and intra-continental deformation [28–30]. To date, systematic studies on ore geology, mineralogy, fluids and isotope geochemistry, and geochronology are still scarce or remain equivocal in the literature, which limits the understanding of the genetic types and metallogenic regularities of the orogenic gold system in the Kalamaili area, East Junggar.

The Nanmingshui gold deposit, situated in the eastern part of the KGB, is a typical medium-sized gold deposit [31], and was discovered in the 1980s with an average grade of 6.1 g/t. Owing to its complex geological features and mineral associations, nearly all published data on this deposit are contentious. Two different views have emerged among geologists regarding the genetic types and metallogenic ages of the Nanmingshui gold deposit. Some advocate a magmatic–hydrothermal model, which is linked to contemporaneous granitic magmatism in the Early Carboniferous (337.5 ± 3.9 Ma) [32]. On the other hand, others propose a metamorphic–hydrothermal model associated with the tectonic transition that occurred in the Kalamaili area during the Late Carboniferous (312.9 ± 4.3 Ma) [23,27]. In this paper, we report new data obtained from field geology, electron microprobe analysis (EMPA) of gold-bearing sulfides, fluid inclusions, H–O isotopic compositions, and the LA-ICP-MS U–Pb dating of hydrothermal zircon in auriferous quartz–tourmaline veins from the Nanmingshui gold deposit. The aims of this study are to examine and define the characteristics and origins of ore fluids, the mechanisms and timing of gold mineralization, and ore genesis in the Nanmingshui gold deposit. Our results provide insights to better understand the gold mineralization and genesis of the Late Paleozoic orogenic gold system in Kalamaili.

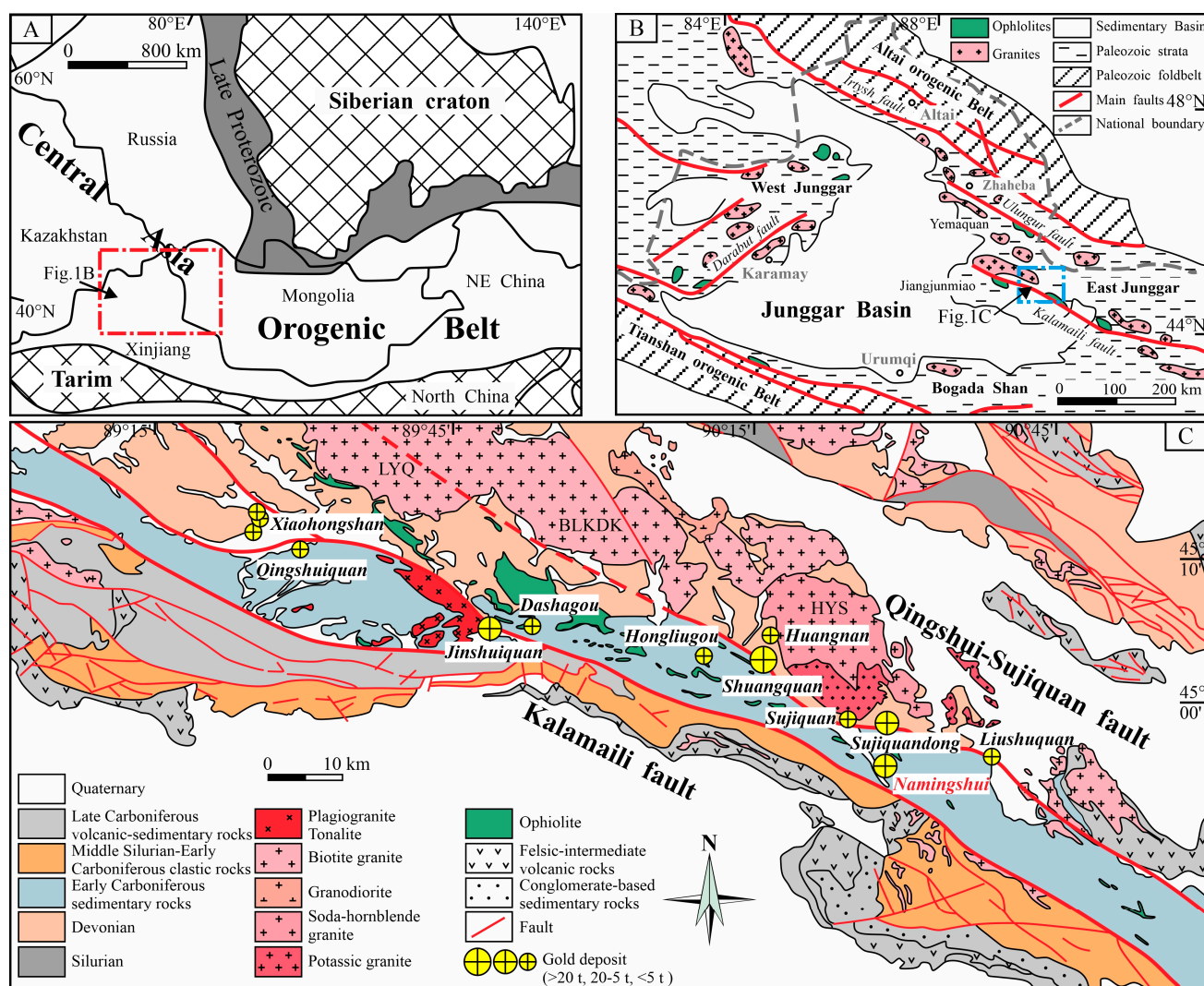


Figure 1. (A) Sketch map of the Central Asian Orogenic Belt, showing the location of the study area (modified from [33]); (B) simplified regional geological map of the Junggar terrane in north Xinjiang (modified from [34,35]); (C) simplified regional geological map of the Kalamaili area, East Junggar (modified from [28]). Abbreviations: LYQ, Laoyaquan; BLKDK, Beilekuduke; HYS, Huangyangshan.

2. Regional Geology

The East Junggar Orogen, Xinjiang, NW China, lying at the junction zone of the Siberian and Kazakhstan–Junggar plates, is part of the CAO and sandwiched between the Zaisan–Erqis (Irtys) fault to the north and the Kalamaili fault to the south. The tectonic units in this region consist, from north to south, of the Dulute–Baytag arc, Yemaquan arc, and Jiangjunmiao accretionary complex (Figure 1B), which are separated from each other by two NW–SE-trending highly deformed and dismembered ophiolite belts (Zhaheba–Aermantai and Kalamaili) [34]. The Kalamaili area lies on the southwestern edge of the Paleozoic East Junggar Orogen, which incorporates three distinct tectonic units from the Late Paleozoic, namely, from north to south, the Yemaquan arc, Kalamaili ophiolite belt (KOB; so-called Kalamaili shear zone or Kalamaili fault zone), and Jiangjunmiao accretionary complex (Figure 1C).

North of the KOB, the Yemaquan arc mainly comprises Devonian to Carboniferous volcanic and volcanosedimentary rocks, and Late Paleozoic post-collisional Alkaline granite plutons [29]. However, several Early Paleozoic intermediate-acid intrusive rocks have been reported in the eastern part of the Yemaquan arc, with zircon LA-ICP-MS U–Pb ages ranging from 427.4 to 418.5 Ma [36]. In the south of the Yemaquan arc, a number of A-type monzogranites, biotite granites, alkali granites, and alkali–feldspar granites are distributed along north of the KOB, the largest of which is the Laoyaquan–Huangyangshan batholith. The zircon U–Pb dating of these plutons, including the Laoyaquan, Beilekuduke, Huangyangshan, and Sujiquan granites, have ages between 311 and 283 Ma, which reveals the end of orogeny and the beginning of intraplate evolution in the Late Carboniferous in the Kalamaili area, East Junggar [37–39]. South of the KOB, the Jiangjunmiao accretionary complex is mainly composed of a well-developed succession of Late Carboniferous clastic sedimentary rocks, and sporadic marine–terrestrial volcanic and carbonate rocks from the Late Silurian.

The NWW-trending KOB, approximately 5–15 km wide, is exposed over a length of nearly 150 km in the Kamst–Hongliugou–Nanmingshui areas to the west and the Zhifang–Aletunkunduo areas to the east [40]. It is primarily composed of fragmented ophiolite mélanges and a heavily deformed volcanic–sedimentary matrix. The rock lithology includes serpentinite, serpentinized peridotite, lherzolite, diabase, gabbro, basalt, plagiogranite, chert, and mafic lava [41], indicating fragments of a paleo-oceanic crust. Recent works gave wide ophiolite ages ranging from 416.7 to 329.9 Ma, with zircon LA-ICP-MS U–Pb ages of gabbro (406 ± 1.8 Ma [42]; 329.9 ± 1.6 Ma [43]) and diabase (416.7 ± 3.2 Ma [44]), and zircon SHRIMP U–Pb ages of plagiogranite (373 ± 10 Ma [45]; 351 ± 6 Ma [46]). The tuff in the Heishantou Formation, unconformably lying over ophiolite mélanges, yielded a zircon LA-ICP-MS U–Pb age of 343.0 ± 5.0 Ma [44], which constrained the upper limit of the emplacement age of the Kalamaili ophiolite. Therefore, the Kalamaili ophiolite, representing one suture between the Kazakhstan–Junggar and Siberian plates, were formed in the period between the Early Devonian and the Early Carboniferous [40].

The KGB investigated in our research is located in the KOB, south of the East Junggar Orogen. Actually, it is an Au–Cu polymetallic belt bounded by the NW–NWW-trending Qingshui–Sujiquan fault to the north and the Kalamaili fault to the south (Figure 1C). The Paleozoic lithologies in this area consist of fore-arc sedimentary rocks of the Devonian to Early Carboniferous, cherts on the ocean floor of the Early Carboniferous, and ophiolite mélanges [28]. From bottom to top, the dominant strata in the KGB include the Middle Devonian Beitashan and Yundukala Formations, and the Lower Carboniferous Jiangbasitao Formation. All of these strata strike northwest and dip to the northeast, and were metamorphosed to zeolite to sub-greenschist facies. As one of two backbone structures, the Kalamaili fault is a high-angle thrust fault that dips to the northeast with angles of 75° – 80° . From east to west, the spatial distribution of this fault is transferred from NWW- to NW-trending and intermittently extends ~300 km with a width of 100–300 m (Figure 1C) [47]. At the northern boundary of the KGB, the Qingshui–Sujiquan fault originates from Qingshuiquan in the west and extends eastwards to the south of Liushuquan via Sujiquan. This NW-trending

thrust fault strikes $280\text{--}300^\circ$ and dips to the north with angles of $60\text{--}80^\circ$, and exceeds 100 km in length and nearly 100 m in width.

More than 100 lode gold deposits, occurrences, and a few placer gold deposits occur in the KGB, most of which (e.g., the Shuangquan, Jinshuiquan, and Nanmingshui lode gold deposits) stretch along the northeastern side of the Kalamaili fault for approximately 400 km [23]. Almost all auriferous quartz $\pm$ tourmaline veins are controlled by the subsidiary NW-NWW- and/or NE-NEE-trending ductile–brittle faults of the Kalamaili shear zone.

3. Deposit Geology

The Nanmingshui gold deposit is located in the eastern segment of the KGB (Figure 1C), several kilometers south of the Qingshui–Sujiquan fault. The exposed lithologies in the mining district are lower-grade metamorphic rocks of the Jiangbasitao Formation that are intensely sheared and foliated, including tuffs, tuffaceous sandstone, basalt, and basaltic andesite (Figure 2). There are 19 auriferous quartz veins identified by the Xinjiang Geology and Mineral Bureau, with average gold grades ranging from 4.12 to 24.19 g/t, which are mined via open pitting and underground operations [31]. Compared with other lode gold deposits in the KGB, tourmaline occurs as a major or minor gangue mineral in most of the gold-bearing veins at Nanmingshui.

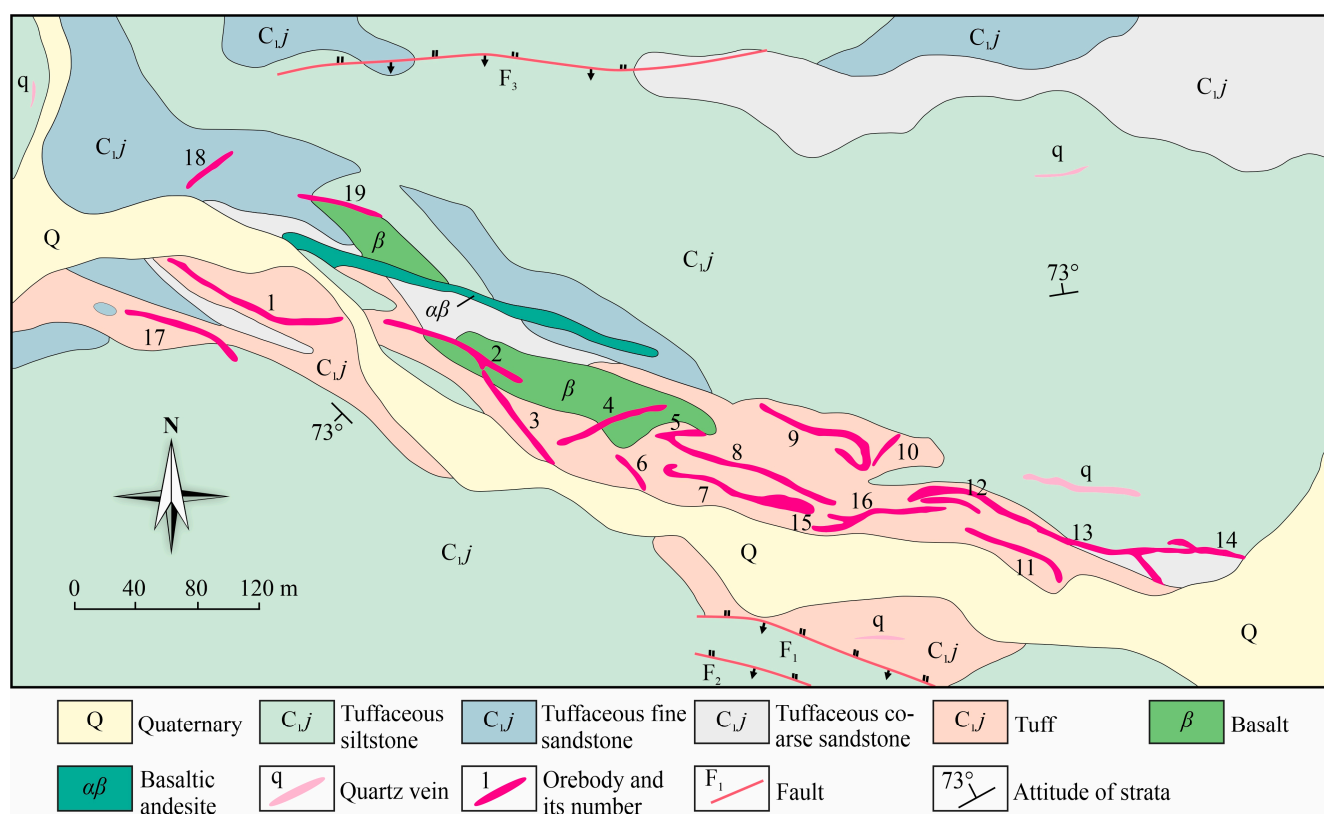


Figure 2. Geological map of the Nanmingshui gold deposit.

3.1. Features of the Ore-Hosting Faults

The spatial distribution of auriferous quartz veins at Nanmingshui is strictly controlled by the NW- to NWW-trending Kalamaili shear zone and its subsidiary ductile–brittle reverse fault systems (Figure 2). On the basis of different orientations, three groups of the subsidiary faults can be identified in the deposit. The first group, consisting of the NW- to NWW-trending faults, strikes $275\text{--}330^\circ$ and dips to the north or southwest with angles of $42\text{--}85^\circ$ (Figure 3A–C). These faults are nearly parallel to the regional faults of the KGB, which are generally 40–400 m in length and 0.3–4.0 m in width. It is noteworthy that the

majority of auriferous quartz–tourmaline veins at Nanmingshui occur in reverse faults. The faults in the second group strike $40\text{--}75^\circ$ and dip to the north, south, or east with angles of $35\text{--}82^\circ$, few of which are exposed in the deposit, with 42–115 m in length and 0.2–6.0 m in width. Only five gold-bearing veins exist in these NE-NEE-trending faults. Both of the groups above belong to pre-metallogenic structures. The nearly EW-trending faults (F1, F2, and F3; Figure 2) of the third group are relatively small in size, and are all post-metallogenic and have no effects on the gold-bearing veins occurring in other faults.

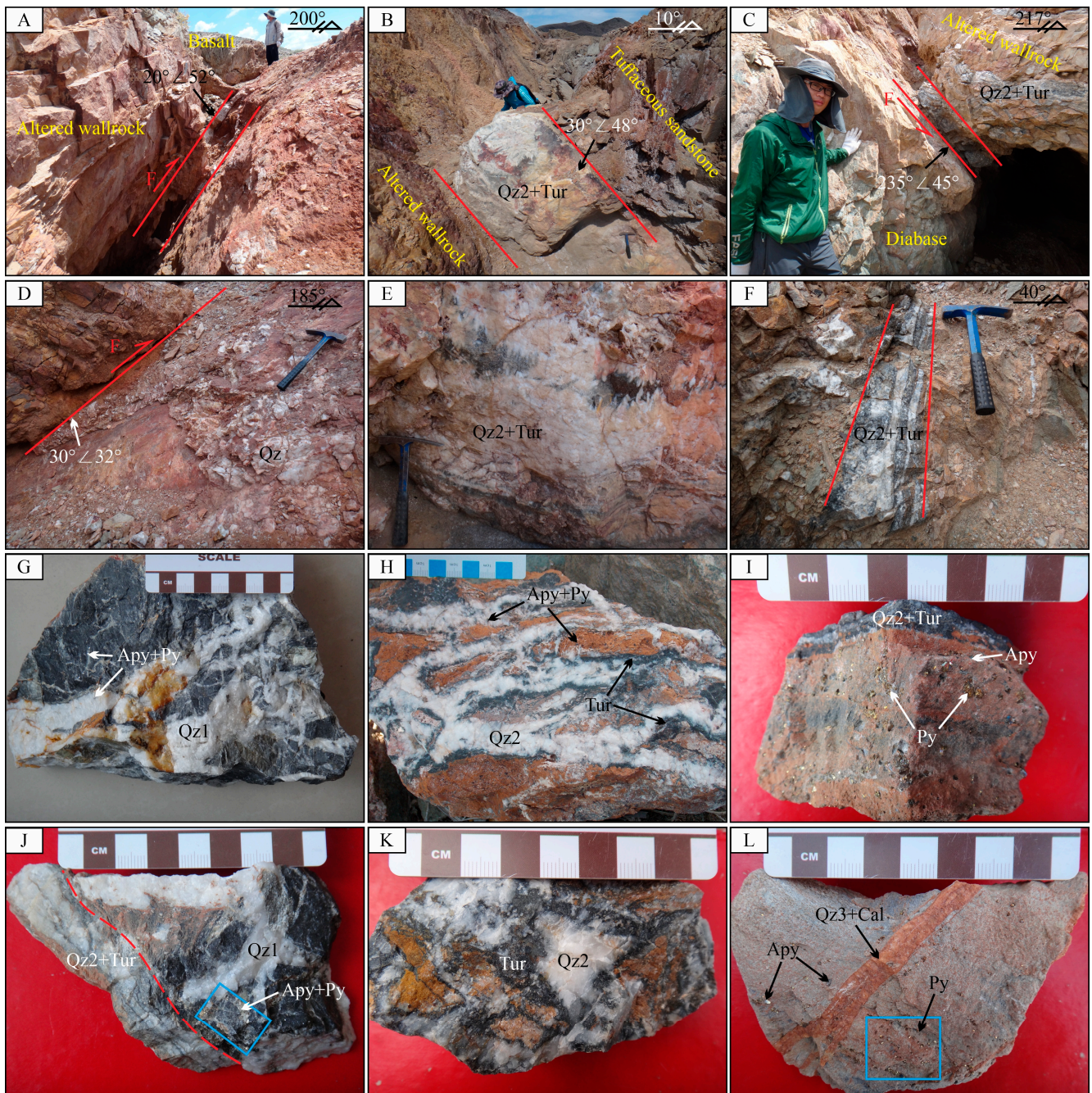


Figure 3. Representative photos of orebodies and various ore types in the Nanmingshui gold deposit. (A) Quartz vein hosted in a high-angle reverse fault, with intensely altered wall-rocks; (B) quartz–tourmaline vein occurring in mylonitic tuffaceous sandstone; (C) auriferous quartz–tourmaline vein

formed in a high-angle reverse fault; (D) limonitized gold-bearing quartz vein near the surface; (E) comb structures in the quartz–tourmaline vein; (F) laminated texture in the quartz–tourmaline vein; (G) scattered and fine-grained pyrite coexisting with arsenopyrite in early-stage milky quartz (Qz1); (H) laminated middle-stage quartz–tourmaline vein (Qz2) containing fine-grained arsenopyrite and pyrite; (I) coarse-grained, cubic or pentagonal–dodecahedral pyrite coexisting with arsenopyrite in the altered rocks; (J) early-stage milky quartz vein (Qz1) crosscut by middle-stage smoky-gray quartz–tourmaline vein (Qz2); (K) middle-stage quartz–tourmaline vein containing several brecciated altered wall-rocks; (L) late-stage quartz–calcite vein (Qz3) intruding in altered rocks. Abbreviations: Apy, arsenopyrite; Py, pyrite; Qz, quartz; Tur, tourmaline; Cal, calcite.

3.2. Characteristics of the Orebodies

The dominant mineralization in the Nanmingshui gold deposit consists of auriferous quartz veins, quartz–tourmaline veins, and subordinately altered rocks (Figure 3A–F). The orebodies typically occur as veins and veinlets, which are lenticular and agglomerated in shape. Among the 19 gold-bearing quartz $\pm$ tourmaline veins, most of them (e.g., Nos. 1, 7, 8, 9, and 13) strike 275–310° and dip to the north or south with variable angles of 21–85° (mostly 40–75°), elongating by 5–145 m with a thickness of 0.15–1.50 m. Other veins (including Nos. 4, 10, 12, and 18) strike 40–70° and dip to the north or south with angles of 42–80°, extending by 5–62 m with a thickness of 0.10–0.45 m (Figure 2). The largest orebody is at the curved part of No. 9, and is mainly composed of quartz–tourmaline veins and altered tuffaceous sandstone (Figure 3B,E). The orebody is 34 m long with an average width of 2 m and a thickness of 1.83 m, and its ore grades vary from 1.55 to 26.24 g/t (mean of 5.40 g/t).

The gold grades of different veins in the Nanmingshui gold deposit vary significantly and mostly range between 4 and 15 g/t. The majority of the orebodies are hosted in high-angle (mainly 40–75°) reverse faults with ductile–brittle deformation (Figure 3A,C). However, all high-grade orebodies are concentrated at sites of structural bends, strike changes, and splays, indicating an important role of vein interconnections for fluid flow and gold precipitation at Nanmingshui [48]. Brecciated and lamellar textures can be found in some quartz–tourmaline veins (Figure 3F,K), which probably show that abrupt fluid–pressure fluctuations from a fault–valve behavior occurred in the process of gold mineralization [49,50].

3.3. Ore Types and Mineral Assemblages

According to the characteristics of mineralization and mineral assemblages, three types of gold ores can be detected in the Nanmingshui gold deposit, including quartz–pyrite ore (Figure 3G), high-grade quartz–tourmaline–gold–polymetallic sulfide ore (Figure 3H), and low-grade altered wall-rock ore (Figure 3I).

The total contents of metallic minerals in different gold ores are commonly less than 5%. The major ore minerals are arsenopyrite and pyrite, while other subordinate species include native gold, chalcopyrite, tetrahedrite, and hematite, containing minor pyrrhotite, galena, and limonite (Figure 4A–I). The non-metallic minerals consist primarily of quartz, tourmaline, sericite, and calcite, with minor amounts of muscovite, chlorite, and epidote (Figure 4J–L). On the basis of morphology, texture, and paragenesis, two generations of pyrite are identified. The early generation of pyrite (Py1) is dominated by micro-grained (0.01–0.10 mm in diameter), euhedral grains exhibiting cubic forms, which occur in isolation in arsenopyrite (Figure 4D,E) or in aggregations in milky quartz veins (Figure 4I). The late generation of pyrite (Py2) mainly consists of fine- to medium-grained (0.2–1.0 mm in diameter) euhedral to subhedral grains, most of which have pentagonal–dodecahedral forms and coexist with arsenopyrite in smoky-gray quartz–tourmaline veins (Figure 4A,B). Many grains of Py2 and coexisting arsenopyrite are fractured or brecciated, showing foam and cataclastic textures with micro-fissures (Figure 4E,F). These textures provide highly favorable conditions for the occurrence of native gold and gold minerals.

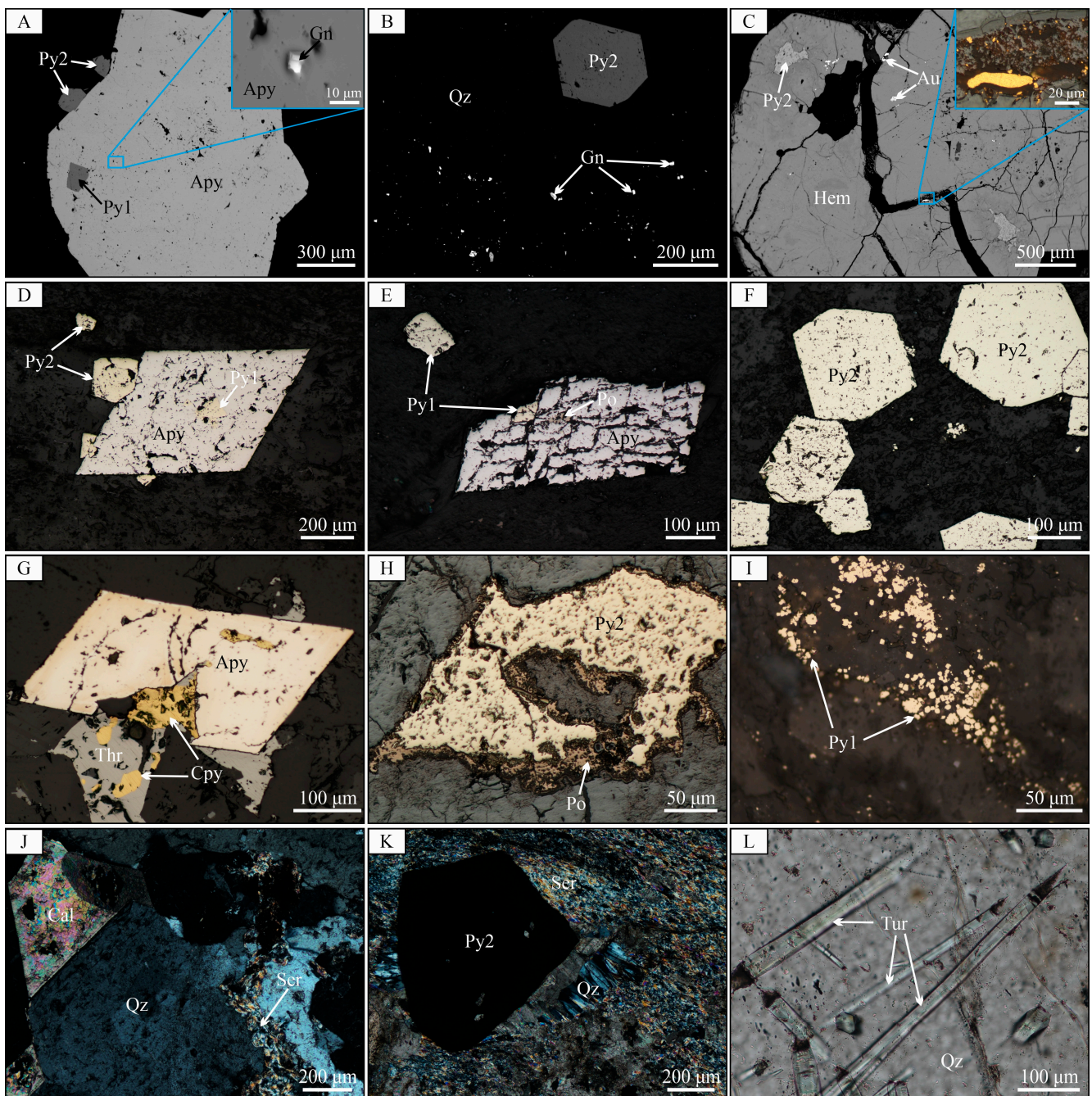


Figure 4. Photomicrographs showing mineral assemblages and textural features in the Nanmingshui gold deposit. (A) Galena and cube-shaped pyrite (Py1) occurring in arsenopyrite as inclusions (BSE); (B) pentagonal–dodecahedral pyrite (Py2) coexisting with fine-grained galena (BSE); (C) irregular native gold occurring in hematite as fissure-filled gold (whole view: BSE, amplified area: reflected light); (D) Py2 coexisting with euhedral arsenopyrite and py1 wrapped in arsenopyrite, displaying a poikilitic texture (reflected light); (E) arsenopyrite with cataclastic texture (reflected light); (F) Py2 occurring as pentagonal-dodecahedral crystals in auriferous quartz–tourmaline veins (reflected light); (G) coexistence of arsenopyrite, chalcopyrite, and tetrahedrite (reflected light); (H) Py2 replaced with pyrrhotite, forming the replacement residual texture (reflected light); (I) Py1 veinlet in quartz vein (reflected light); (J) quartz coexisting with sericite and calcite (transmitted light); (K) fibrous sericite and quartz around Py2, forming a pressure shadow structure (transmitted light); (L) acicular tourmaline coexisting with smoky-gray quartz (transmitted light). Abbreviations: Ser, Sericite; Gn, galena; Cpy, chalcopyrite; Thr, tetrahedrite; Po, pyrrhotite; Hem, hematite; Au, native gold. For other abbreviations, see Figure 3.

The ores are mainly characterized by disseminated, vein-stockwork, brecciated, or veinlet structures (Figure 3G–K). Minerals occur as euhedral to subhedral or anhedral crystals. Metasomatic, cataclastic, and pressure-shadow textures are commonly observed, indicating that the Nanmingshui gold deposit was formed as a result of hydrothermal replacement (Figure 4).

3.4. Mineralization Stages and Wall-Rock Alteration

Based on the crosscutting relationships and mineral assemblages, gold mineralization can be divided into three stages. These are the quartz–pyrite–minor native gold (early) stage, the quartz–tourmaline–arsenopyrite–pyrite–gold–polymetallic sulfide (middle or main) stage, and the quartz–calcite (late) stage. The paragenetic sequence is illustrated in Figure 5.

Stage Mineral	Early stage	Middle stage	Late stage
Pyrite 1	—	—	
Galena		---	
Arsenopyrite	—	—	
Pyrite 2		—	
Native gold	---	—	
Pyrrhotite		-----	
Chalcopyrite		—	
Tetrahedrite		—	
Hematite			—
Limonite			—
Quartz	—	—	—
Tourmaline		—	
Sericite		—	—
Chlorite		-----	
Epidote		-----	
Calcite			—

Figure 5. Mineral paragenesis of the Nanmingshui gold deposit. The dotted line represents trace amounts of that mineral and the thickness of the solid line represents the amount of that mineral.

The early-stage veins primarily consist of quartz, pyrite, and minor native gold, with widths ranging from less than 10 cm to 2 m. Quartz commonly coexists with py1 and minor fissure-filled native gold in the milky or whitish veins (Figure 3G), which are always intersected by the auriferous quartz–tourmaline veins (Figure 3J). In the middle-stage veins, hydrothermal minerals dominantly include quartz, tourmaline, native gold, arsenopyrite, and pyrite, with minor chalcopyrite, tetrahedrite, pyrrhotite, and galena. Quartz of this stage is typically smoky gray in color, and occurs as veins with a width of 0.2–2.0 m. It is

commonly coherent with euhedral to subhedral arsenopyrite and pentagonal-dodecahedral pyrite, as well as native gold, chalcopyrite, tetrahedrite, and other sulfides. Tourmaline is a major or minor gangue mineral in gold-bearing veins, and occurs in the form of acicular crystals and veinlets and is visible in hand specimens (Figure 3H). Polymetallic sulfides generally occur as dissemination (Figure 3I) or veinlets (Figure 4I), while the native gold is exclusively confined to granular inclusions and fissure-filled gold (Figure 4C) in the auriferous veins. Late-stage veinlets mainly consist of white quartz and calcite, without any gold minerals observed, and are generally 2–5 cm in width. These barren quartz–calcite veinlets are always filled in the fractures of altered wall-rocks (Figure 3L) and crosscut the earlier gold-bearing veins.

The extensive wall-rock alteration at Nanmingshui is characterized by the hydrothermal minerals of quartz, sulfides, sericite, calcite, chlorite, and epidote in the alteration zone. Based on our field investigations, an intense lateral alteration is symmetrically distributed at the point of contact between gold-bearing veins and wall-rocks. From the center to the outside, the alteration zonation is as follows: (1) auriferous quartz–tourmaline–polymetallic sulfide veins; (2) altered wall-rocks with silicification, arsenopyritization, pyritization, and sericitization that occur in the proximal zone (approximately 5–20 m in width); (3) altered wall-rocks with alteration types of sericitization, carbonatization, chloritization, and rare epidotization in the distal zone; and (4) unaltered wall-rocks on the outermost side.

4. Samples and Analytical Methods

In this study, more than 50 representative samples were collected from field outcrops and mine dumps at Nanmingshui. Samples for electron probe microanalysis (EPMA), hydrogen and oxygen (H-O) isotopes, and zircon U-Pb dating were collected from the middle-stage quartz–tourmaline–gold–polymetallic sulfide veins. Others for the fluid inclusion study were selected from the auriferous and barren veins of the three different stages.

4.1. EPMA and Mapping

Twelve samples were double-side-polished as thin sections of 0.1 mm thickness for optical microscopy and EPMA. Backscattered electron (BSE) images were taken and the chemical compositions of the minerals (native gold and sulfides) were determined using a JEOL JXA-8230 Electron Probe Micro-Analyzer under the operation conditions of 15 kV, 20 nA, a beam size of 2 μm in diameter, and count times of 10–40 s (peak) and 5–20 s (backgrounds) at the Shandong Analysis Center of the China Metallurgical Geology Bureau (SAC-CMGB). The characteristic X-rays used were Fe(K α), S (K α), As (L α), Au (M α), Ag (L α), Ni (K α), Co (K α), Cu (K α), Zn (K α), Sb (L α), Se (L α), Te (L α), Cd (L α), Pb (M α), Hg (M α), and Bi (M α). The standard materials for each element were as follows: native metal standards for Au, Ag, Ni, Cd, and Bi; pyrite (FeS₂) for Fe and S; cuprite (Cu₂O) for Cu; galena (PbS) for Pb; sphalerite (ZnS) for Zn; bismuth selenide (Bi₂Se₃) for Se; modderite (CoAs) for Co and As; and stibnite (Sb₂S₃) for Sb. The analysis yielded an accuracy of 1–5%. The average detection limits obtained in this study were 184 ppm for Fe, 98 ppm for S, 142 ppm for As, 157 ppm for Au, 79 ppm for Ag, 116 ppm for Ni, 133 ppm for Co, 266 ppm for Cu, 185 ppm for Zn, 101 ppm for Sb, 113 ppm for Se, 115 ppm for Te, 149 ppm for Cd, 304 ppm for Pb, and 252 ppm for Bi. Matrix effects were corrected using the ZAF (Atomic-Number–Absorption–Fluorescence) correction program.

Trace element mapping was performed at the Research Center of Genetic Mineralogy, China University of Geosciences, Beijing (RCGM-CUGB), using Tescan MIRA3-XMU scanning electron microscope (SEM) equipped with an X-ray energy-dispersive spectrometer (EDS) of Oxford INCA Energy X-Max 20. The EDS X-ray elemental maps were collected at 20 kV with a working distance of 15 mm, a probe current of 83 μA , and a dwell time of 500 μs for acquisition at each point. Maps are up to 1024 $\times$ 1024 pixels in size.

4.2. Fluid Inclusion Study

Double-polished thin sections (0.2 mm thick) were made from more than 20 quartz samples for petrographic observation, which were used to identify the genesis, types, and vapor/liquid ratios of the fluid inclusions (FIs). Fourteen representative samples were selected for microthermometry and laser Raman spectroscopy analyses.

Microthermometric measurements of the FIs were performed using a Linkam THMSG-600 heating/freezing stage (from -196 to $+600$ °C) at the Ore Deposit Geochemistry Microanalysis Laboratory, State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Beijing (ODGML-SKL-CUGB). The stage was calibrated by measuring the triple point of pure CO_2 (-56.6 °C) and the freezing point of pure water (0 °C) in synthetic FIs. The estimated accuracy of the measurement was about ± 0.1 °C during the cooling runs and ± 2 °C during the heating runs, relative to the standard material. The heating and cooling rates were generally less than 20 °C/min, and reduced to 0.2 °C/min near the phase transitions. FIs were first quickly cooled to/below -100 °C, and then, heated progressively to obtain the temperatures of the phase transitions, including the melting temperature of solid CO_2 ($T_{\text{m-CO}_2}$), the temperature of final ice melting ($T_{\text{m-ice}}$), the temperature of CO_2 -clathrate dissociation ($T_{\text{m-cla}}$), the partial homogenization temperature of the CO_2 phase ($T_{\text{h-CO}_2}$), and the total homogenization temperature (T_{h}). The salinities of aqueous FIs were calculated using the equations for the $\text{NaCl-H}_2\text{O}$ system [51]. The W - ρ - X - P parameters (salinity–density–mole fraction–pressure) were calculated from microthermometric data using the Flicor program [52,53].

The gas compositions in a single fluid inclusion were analyzed using a LabRAM HR800 Raman spectrometer (Horiba Jobin Yvon) at the Analytical Laboratory of the Beijing Research Institute of Uranium Geology (BRIUG). The detecting conditions were as follows: a tunable argon ion laser with a wavelength of 532 nm, laser power up to 50 mW, a spectral resolution of 1.5 cm^{-1} , and a spatial resolution of 1 μm . The spectral range fell between 100 and 4300 cm^{-1} for the analysis of CO_2 , CH_4 , N_2 , and H_2O in the vapor and liquid phases.

4.3. H-O Isotope Analyses

The H-O isotope compositions of FIs in auriferous quartz were analyzed using a Finnigan MAT253-type mass spectrometer at the Analytical Laboratory of BRIUG, following the methods in reference [54]. Oxygen gas was liberated from the samples via a quantitative reaction with BrF_5 in externally heated nickel vessels. Hydrogen was measured by reacting the H_2O extracted from the FIs with zinc at 550 °C. The Standard Mean Ocean Water (SMOW) was adopted as the standard for oxygen and hydrogen, with total uncertainties of $\pm 0.2\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 1\text{‰}$ for δD . The $\delta^{18}\text{O}_{\text{water}}$ values were calculated using the fractionation formula in reference [55].

4.4. Zircon U-Pb Dating

Approximately 20 kg fresh sample was collected from the auriferous quartz–tourmaline vein for zircon U-Pb dating. Zircon grains were separated using conventional crushing, heavy liquid, and magnetic separation techniques, and then, hand-picked under a binocular microscope. They were mounted in epoxy resin and polished to approximately half thickness. Representative zircon grains were prepared for cathodoluminescence (CL) investigations to expose the internal textures and guide U-Pb dating.

Zircon U-Pb dating and rare earth element (REE) analyses were conducted using a Thermo Fisher's X-series II ICP-MS instrument connected to a Coherent GeoLasPro-193 nm laser (LA-ICP-MS) at the ODGML-SKL-CUGB. Helium was applied as the carrier gas and mixed with argon prior to entering the ICP-MS torch. The diameter of the laser spot was 32 μm with a 6 Hz laser pulse repetition rate. Zircon 91500 and NIST610 were used as the external standards for the U-Th-Pb isotopic ratios and rare earth element concentration, respectively. Meanwhile, zircon Plešovice was used as a monitoring standard for each analysis [56]. Time-dependent drifts of U-Th-Pb isotopic ratios were corrected using linear interpolation over time for every five analyses, according to the variations in the 91500

standard. For each analysis, 20 s of background was acquired for each analysis followed by 50 s of sample signal. Quantitative calibration for rare earth element concentrations and zircon U-Pb ages was carried out using ICPMSDataCal 10.7 software [57]. Data reduction and Concordia diagrams were processed using the ISOPLOT 4.15 program [58].

5. Results

5.1. Chemical Compositions of Native Gold and Sulfides

The EPMA data and mapping of ore minerals from the Nanmingshui gold deposit are shown in Table 1 and Figure 6, respectively. The gold and silver contents at the three points of gold grains are 89.35–90.51 wt.% (mean of 89.82 wt.%) and 2.81–3.08 wt.% (mean of 2.95 wt.%), respectively, similar to the chemical compositions of native gold ($\text{Au} > 80 \text{ wt.}\%$) [59]. The calculated gold fineness, expressed as $1000 \text{ Au}/(\text{Au} + \text{Ag} + \text{Hg})$, has a narrow range from 941 to 944 (mean of 943). However, high Hg (up to 2.56 wt.%) and low Cu (0.03–0.06 wt.%) contents of native gold are typically consistent with hydrothermal α -phase Au-Ag-Hg alloys [60]. The average contents of the trace elements Fe, S, and Bi in these gold minerals are 0.77 wt.%, 0.01 wt.%, and 0.97 wt.%, respectively, whereas the contents of other minor elements (As, Pb, Sb, Zn, Ni, Co, and Te) are rarely detected or below the detection limit.

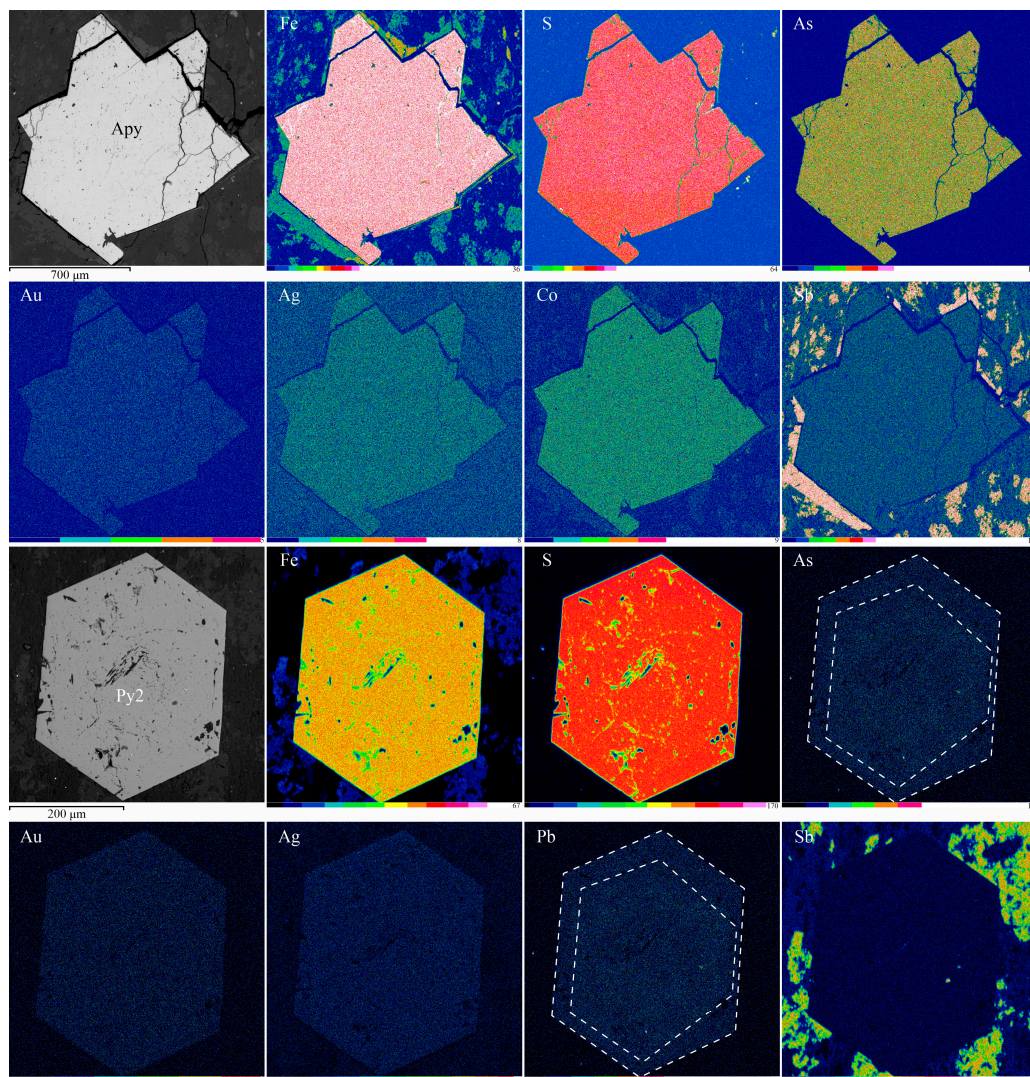


Figure 6. BSE images along with EDS X-ray compositional maps for Apy and Py2 in the auriferous quartz veins of the middle stage at Nanmingshui. The X-ray lines used were $K\alpha$ for As and $L\alpha$ for Pb, respectively.

Table 1. Electron probe data of native gold and sulfides in the Nanmingshui gold deposit.

Mineral	Se	Cd	Au	Ag	As	Fe	S	Cu	Pb	Sb	Zn	Ni	Co	Hg	Te	Bi	Total
Ng (<i>n</i> = 3)																	
Min			89.35	2.81	bdl	0.49	0.01	0.03	bdl	bdl	bdl	bdl	bdl	2.42	bdl	0.78	96.89
Max	wt. %		90.51	3.08	0.01	1.30	0.02	0.06	bdl	0.02	0.02	bdl	0.02	2.56	0.04	1.29	97.26
Avg			89.82	2.95	0.01	0.77	0.01	0.04	bdl	0.01	0.01	bdl	0.01	2.50	0.01	0.97	97.10
Min			0.87	0.05	bdl	0.02	0.00	0.00	bdl	bdl	bdl	bdl	bdl	0.02	bdl	0.01	1.00
Max	at. %		0.90	0.05	0.00	0.04	0.00	0.00	bdl	0.00	0.00	bdl	0.00	0.02	0.00	0.01	1.00
Avg			0.88	0.05	0.00	0.03	0.00	0.00	bdl	0.00	0.00	bdl	0.00	0.02	0.00	0.01	1.00
Apy (<i>n</i> = 8)																	
Min	0.20	bdl	bdl	bdl	39.84	35.53	21.21	bdl	bdl	bdl	bdl	bdl	0.03				98.26
Max	wt. %	0.27	0.03	0.01	0.02	41.38	36.45	22.39	0.01	0.08	0.08	0.03	0.02	0.06			99.35
Avg	0.23	0.01	0.00	0.01	40.45	35.93	22.02	0.00	0.02	0.02	0.01	0.01	0.05				98.75
Min	0.00	bdl	bdl	bdl	0.85	1.02	1.07	bdl	bdl	bdl	bdl	bdl	0.00				3.00
Max	at. %	0.01	0.00	0.00	0.00	0.89	1.04	1.12	0.00	0.00	0.00	0.00	0.00	0.00			3.00
Avg	0.00	0.00	0.00	0.00	0.86	1.03	1.10	0.00	0.00	0.00	0.00	0.00	0.00				3.00
Formula Fe _{1.03} As _{0.86} S _{1.10} (to 3 atoms p.f.u.)																	
Py2 (<i>n</i> = 10)																	
Min	bdl	bdl	bdl	bdl	0.51	45.64	52.34	bdl	bdl	bdl	bdl	bdl	bdl				99.44
Max	wt. %	0.01	0.02	0.08	0.01	1.96	46.66	53.68	0.05	0.12	0.02	0.03	0.28	0.15			101.11
Avg	0.00	0.01	0.02	0.00	1.21	46.05	52.78	0.01	0.04	0.00	0.01	0.05	0.07				100.25
Min	bdl	bdl	bdl	bdl	0.01	0.99	1.97	bdl	bdl	bdl	bdl	bdl	bdl				3.00
Max	at. %	0.00	0.00	0.00	0.03	1.00	2.00	0.00	0.00	0.00	0.00	0.01	0.00				3.00
Avg	0.00	0.00	0.00	0.00	0.02	0.99	1.98	0.00	0.00	0.00	0.00	0.00	0.00				3.00
Formula Fe _{0.99} S _{1.98} (to 3 atoms p.f.u.)																	
Cpy (<i>n</i> = 10)																	
Min	bdl	bdl	bdl	0.00	bdl	27.27	33.54	32.06	0.00	bdl	0.01	bdl	0.04				97.90
Max	wt. %	0.05	0.03	0.05	0.03	31.05	34.73	35.93	0.10	0.12	1.52	0.01	0.07				99.48
Avg	0.01	0.01	0.01	0.02	0.01	29.24	34.30	34.45	0.04	0.05	0.38	0.00	0.05				98.57
Min	bdl	bdl	bdl	0.00	bdl	0.92	1.98	0.94	0.00	bdl	0.00	bdl	0.00				4.00
Max	at. %	0.00	0.00	0.00	0.00	1.04	2.02	1.07	0.00	0.00	0.04	0.00	0.00				4.00
Avg	0.00	0.00	0.00	0.00	0.00	0.98	2.00	1.01	0.00	0.00	0.01	0.00	0.00				4.00
Formula Cu _{1.01} Fe _{0.98} S _{2.00} (to 4 atoms p.f.u.)																	

Note: bdl denotes the detection limit. Abbreviations: Ng, native gold; Min, minimum; Max, maximum; Avg, average. For other abbreviations, see Figure 3.

The EDS maps of most elements, such as Fe, S, As, Au, Ag, Co, and Sb, in arsenopyrite display a nearly homogeneous distribution, with depletion in Au, Ag, and Sb and relative enrichment in Fe, S, As, and Co (Figure 6). Both the major and trace element compositions are slightly variable in arsenopyrite. Compared to the theoretical compositions (34.30 wt.% Fe, 46.01 wt.% As, and 19.69 wt.% S), eight arsenopyrite grains are intensely depleted in As and enriched in Fe and S, with the As, Fe, and S contents in the ranges of 39.84–41.38 wt.% (mean of 40.45 wt.%), 35.53–36.45 wt.% (mean of 35.93 wt.%), and 21.21–22.39 wt.% (mean of 22.02 wt.%), respectively. Only minor amounts of trace elements such as Se (0.20–0.27 wt.%) and Co (0.03–0.06 wt.%) are present in the analyzed arsenopyrite grains. However, the majority of the contents of other elements, such as Au, Ag, Cu, Pb, Sb, Zn, and Ni, vary from below the limit of detection (bdl) to less than 0.03 wt.%. The calculated formula of arsenopyrite is Fe_{1.03}As_{0.86}S_{1.10}.

In the EDS maps of Py2, most elements (e.g., Fe, S, Au, Ag, and Sb) show a relatively homogeneous distribution, whereas As and Pb are slightly richer in the rims than in the cores. The Pb and S maps indicate that some galena inclusions occur in Py2 (Figure 6). For Py2, the Fe and S contents are 45.64–46.66 wt.% (mean of 46.05 wt.%) and 52.34–53.68 wt.% (mean of 52.78 wt.%), respectively. The As contents in these pyrites vary between 0.51 and 1.96 wt.% with an average of 1.21 wt.%, whereas the corresponding Au contents vary from bdl to 0.08 wt.%, which are similar to the compositions of gold-bearing arsenian pyrite [61]. The contents of Pb (bdl to 0.12 wt.%), Co (bdl to 0.15 wt.%), and Ni (bdl to 0.28 wt.%) in Py2 are higher than the detection limit and vary greatly, but the contents of other trace elements (Se, Cd, Ag, Cu, Sb, and Zn) are relatively low (Figure 6). The calculated formula of Py2 (Fe_{0.99}S_{1.98}) is near the theoretical composition (Table 1).

The contents of major elements in chalcopyrite vary more greatly than those in other sulfides, with Cu, Fe, and S contents of 32.06–35.93 wt.% (mean of 34.45 wt.%),

27.27–31.05 wt.% (mean of 29.24 wt.%), and 33.54–34.73 wt.% (mean of 34.30 wt.%). The contents of trace elements are below 0.05 wt.%, except for Pb (bdl to 0.10 wt.%), Sb (bdl to 0.12 wt.%), Zn (0.01 to 1.52 wt.%), and Co (0.04 to 0.07 wt.%). In particular, the Au contents at the 10 analyzed points range from bdl to 0.05 wt.%. Based on the EPMA data (Table 1), the calculated chalcopyrite formula is $\text{Cu}_{1.01}\text{Fe}_{0.98}\text{S}_{2.00}$, which is the same as the theoretical composition.

5.2. Fluid Inclusion Geochemistry

5.2.1. Petrography and Classification

The FIs in quartz at the three stages of the veins at Nanmingshui are relatively large in size (3–22 μm) and rich in numbers. The vast majority are primary inclusions; however, pseudosecondary FIs are visible along the healing fractures that do not cut across the quartz crystal boundaries. Through phase relationships at room temperature (25 °C), phase transitions during heating and cooling, and compositional data from the Raman spectroscopic analysis, three types of FIs were identified: $\text{H}_2\text{O}-\text{CO}_2$ or aqueous–carbonic (C-type), aqueous (W-type), and pure CO_2 or carbonic (PC-type) FIs (Figure 7), in decreasing order of their abundance.

C-type ($\text{H}_2\text{O}-\text{CO}_2-\text{NaCl} \pm \text{CH}_4 \pm \text{N}_2$) is the most predominant FI in the early- and middle-stage quartz, accounting for as much as 60% of the total FIs. These FIs consist of two (liquid CO_2 + liquid H_2O) or three phases (vapor CO_2 + liquid CO_2 + liquid H_2O) at room temperature, and comprise CO_2 - H_2O - NaCl FIs (type Ia) with the CO_2 phase occupying 20–45% (mostly 25–40%) of the total inclusion volume (Figure 7A,D–G) and CO_2 -rich inclusions (type Ib) with the CO_2 phase accounting for 50–80 vol.% (Figure 7H,I). When the temperature is cooled down to 20 °C or below during the freezing run, vapor CO_2 can also be observed in two phases of the C-type FIs. C-type inclusions usually occur as single isolated inclusions or as clusters along the growth zones of quartz grains, most of which have negative crystal, ellipsoidal, and a variety of polygonal or rare irregular shapes with sizes ranging from 4 to 20 μm . The coexistence of C- and PC- or W-type FIs can often be observed in the same crystal (Figure 7A,E,F).

W-type ($\text{H}_2\text{O}-\text{NaCl}$) FIs are commonly captured in quartz of all three stages of veins, accounting for 30% of the total FI population, but their abundance at the early, middle, and late stages shows an increasing trend. Especially in the quartz crystals of late stage, it is the only type of FI that can be identified. W-type inclusions usually appear as two-phase (liquid H_2O + vapor H_2O) aqueous FIs without a visible CO_2 phase (Figure 7C) at room temperature. The vapor phase occupies 15–70 vol.% (mostly 15–30 vol.%) of the total inclusion volume, but some inclusions occur as monophasic (liquid H_2O or vapor H_2O) aqueous inclusions individually (Figure 7B). The majority of them occur in isolation or as clusters or trails within quartz crystals, and generally show negative crystal or subrounded-oval shapes with sizes of 3–15 μm . Sometimes, W-type FIs coexist with C- or PC-type inclusions in quartz crystals of the early and middle stages (Figure 7A,F).

PC-type FIs can only be observed in quartz of the early and middle stages and account for less than 10% of the total FIs. All of these FIs consist of almost pure carbonic fluid at room temperature, including two-phase CO_2 (vapor CO_2 + liquid CO_2) and monophasic CO_2 (liquid CO_2). Only when the temperature is cooled down to 15 °C can vapor CO_2 in the monophasic CO_2 of PC-type FIs be visible. They generally appear as isolated singles and show oval, negative crystal, or irregular shapes with sizes varying from 4 to 8 μm . PC-type always coexist with C-type FIs in the same field of petrographic view (Figure 7A,E), and rarely with the W-type FIs (Figure 7B).

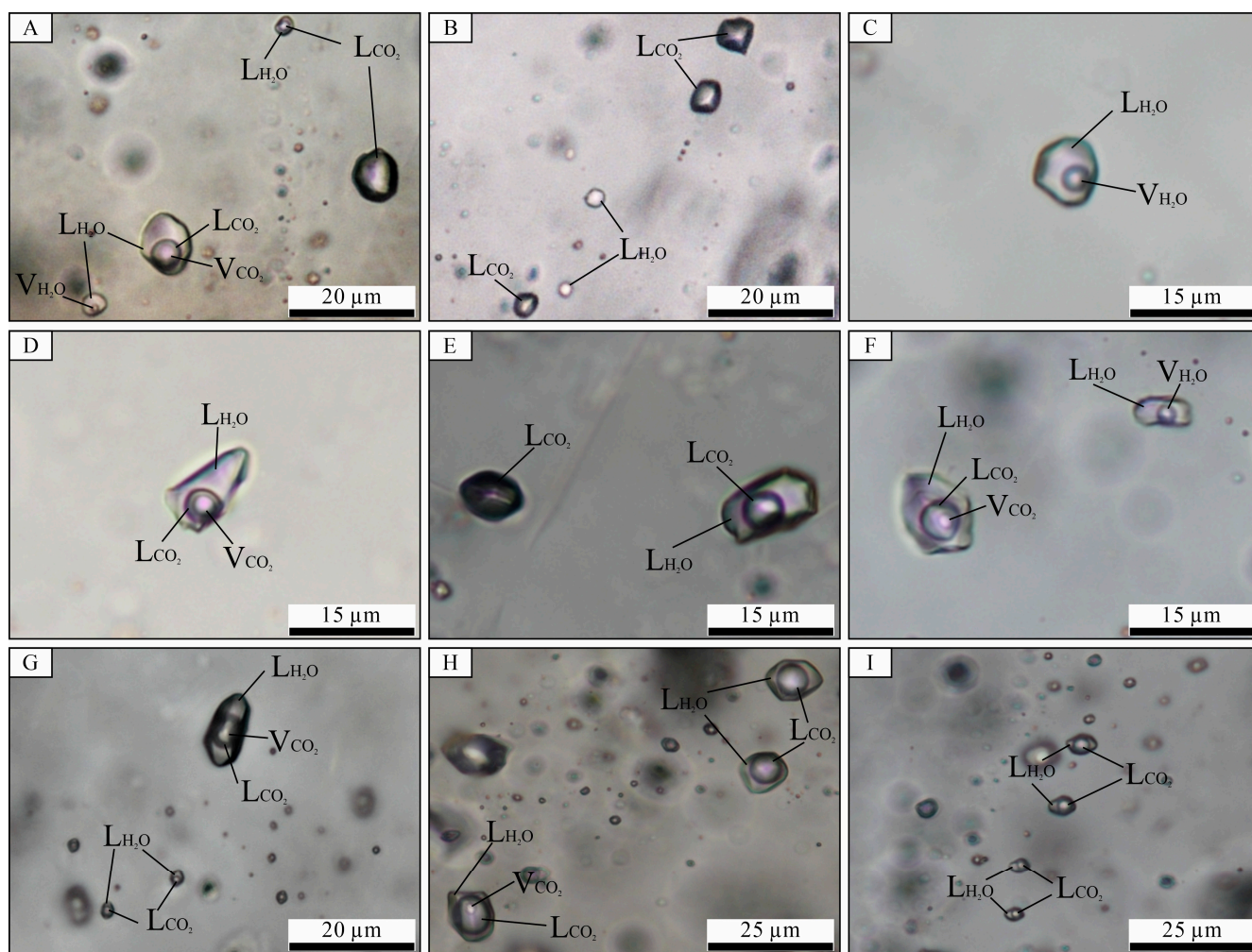


Figure 7. Microphotographs showing the major fluid inclusion types in quartz from the Nanmingshui gold deposit. (A) Coexistence of the C-type, W-type, and PC-type FIs in the early-stage quartz; (B) coexistence of the PC-type and W-type FIs in the early-stage quartz; (C) W-type inclusion in the late-stage quartz; (D) C-type inclusion in the middle-stage quartz; (E) coexistence of the C-type and PC-type FIs in the middle-stage quartz; (F) coexistence of the C-type and W-type fluid inclusions in the middle-stage quartz; (G) coexistence of the type Ia and Ib FIs in the middle-stage quartz; (H) Ib-type FIs in the middle-stage quartz; (I) C-type FIs in the middle-stage quartz with negative crystal shape. Abbreviations: VCO₂, vapor CO₂; LCO₂, liquid CO₂; VH₂O, vapor H₂O; LH₂O, liquid H₂O.

5.2.2. Microthermometry

The microthermometric data of all three types of FIs from the early-, middle-, and late-stage veins at Nanmingshui are shown in Table 2 and Figures 8 and 9.

Early stage: C-type FIs with a small number of W-type inclusions were observed as primary inclusions in the early-stage veins. The C-type FIs freeze to a solid phase below $-100\text{ }^{\circ}\text{C}$ during cooling runs. Their melting temperatures of solid CO₂ ($T_{m\text{-CO}_2}$) occur between -58.2 and $-57.4\text{ }^{\circ}\text{C}$ (mean of $-57.8\text{ }^{\circ}\text{C}$), lower than the triple point of pure CO₂ ($-56.6\text{ }^{\circ}\text{C}$; Figure 9A), implying the presence of minor additional gases (mostly like CH₄ and/or N₂). The melting temperatures of CO₂ clathrate ($T_{m\text{-cla}}$) are between 8.9 and $9.8\text{ }^{\circ}\text{C}$ (mean of $9.5\text{ }^{\circ}\text{C}$; Figure 9B), and these values are representative of lower salinities varying from 0.4 to $2.2\text{ wt.}\%$ NaCl eqv. (mean of $1.1\text{ wt.}\%$ NaCl eqv.). The partial homogenization temperatures of the CO₂ phases ($T_{h\text{-CO}_2}$) range from 18.8 to $29.9\text{ }^{\circ}\text{C}$ (mostly between 22.0 and $24.0\text{ }^{\circ}\text{C}$ and with a mean of $23.6\text{ }^{\circ}\text{C}$; Figure 9C) and all of them are homogenized to liquid CO₂. The C-type inclusions are totally homogenized (T_h) to

aqueous phases at temperatures from 257 to 339 °C, peaking at 280–320 °C (mean of 298 °C). However, a few inclusions decrepitate prior to final homogenization at 238–334 °C. The calculated molar fractions of CO₂ (X_{CO_2}) range from 0.11 to 0.31 (mean of 0.15), while the densities of the CO₂ (ρ_{CO_2}) phase range from 0.60 to 0.79 g/cm³ (mean of 0.73 g/cm³) and the bulk densities (ρ_{total}) range from 0.80 to 1.01 g/cm³ (mean of 0.91 g/cm³). The microthermometric analyses of W-type FIs show that the final ice-melting temperatures ($T_{\text{m-ice}}$) occur between −2.2 and −1.5 °C (mean of −1.9 °C), equivalent to salinities of 2.6 to 3.7 wt.% NaCl eqv. (mean of 3.2 wt.% NaCl eqv.). The total homogenization of W-type inclusions (to liquid H₂O) shows a wide temperature range from 220 to 338 °C, with the majority clustering at 260–320 °C (mean of 276 °C). Their ρ_{total} values are within the range of 0.66–0.87 g/cm³ (mean of 0.77 g/cm³).

Table 2. Microthermometric data of fluid inclusions in quartz from the Nanmingshui gold deposit.

Stage/Type	Range	Vapor (vol.%)	X_{CO_2}	$T_{\text{m-CO}_2}$ (°C)	$T_{\text{m-cla}}$ (°C)	$T_{\text{h-CO}_2}$ (°C)	$T_{\text{m-ice}}$ (°C)	T_{h} (°C)	Salinity (wt.% NaCl eqv.)	ρ_{CO_2} (g/cm ³)	ρ_{total} (g/cm ³)
Early stage											
C-type	Min	30	0.11	−58.2	8.9	18.8		257	0.4	0.60	0.80
	Max	60	0.31	−57.4	9.8	29.9		339	2.2	0.79	1.01
	Avg	36	0.15	−57.8	9.5	23.6		298	1.1	0.73	0.91
	<i>n</i>	19	18	10	15	18		19	15	18	18
W-type	Min	20					−2.2	220	2.6		0.66
	Max	30					−1.5	338	3.7		0.87
	Avg	26					−1.9	276	3.2		0.77
	<i>n</i>	9					7	9	7		7
Middle stage											
C-type	Min	20	0.07	−62.2	7.5	12.9		209	0.4	0.66	0.82
	Max	80	0.58	−56.0	9.8	28.8		361	4.8	0.84	0.99
	Avg	38	0.16	−58.3	9.0	22.5		277	2.0	0.74	0.91
	<i>n</i>	69	69	36	64	69		69	64	69	69
W-type	Min	15					−3.7	190	0.9		0.69
	Max	70					−0.5	349	6.0		0.91
	Avg	25					−2.2	249	3.6		0.82
	<i>n</i>	125					95	125	95		95
PC-type	Min	10		−61.5		12.3				0.80	
	Max	30		−57.2		19.0				0.86	
	Avg	21		−59.0		16.1				0.82	
	<i>n</i>	7		7		7				7	
Late stage											
W-type	Min	15					−4.3	172	1.4		0.79
	Max	35					−0.8	287	6.9		0.95
	Avg	23					−1.8	213	3.0		0.88
	<i>n</i>	51					31	51	31		31

Middle stage: All three types of FIs were identified in the middle-stage quartz. For the most abundant C-type FIs, the $T_{\text{m-CO}_2}$ values during the heating runs range from −62.2 to −56.0 °C (mean of −58.3 °C; Figure 9A), and are slightly below the triple point of pure CO₂. The $T_{\text{m-cla}}$ values of C-type inclusions are in a narrow range of 7.5–9.8 °C (mean of 9.0 °C; Figure 9B), corresponding to salinities between 0.4 and 4.8 wt.% NaCl eqv. (mean of 2.0 wt.% NaCl eqv.). The CO₂ phases homogenize to a liquid at temperatures of 12.9–28.8 °C (mainly between 18.0 and 26.0 °C; Figure 9C). C-type inclusions in the middle-stage quartz contain a ρ_{CO_2} of 0.66–0.84 g/cm³ (mean of 0.74 g/cm³) and a ρ_{total} of 0.82–0.99 g/cm³ (mean of 0.91 g/cm³), with X_{CO_2} ranging from 0.07 to 0.58 (mean of 0.16). These inclusions homogenize into both liquid and vapor states between 209 and 361 °C, with most clustering at 260–300 °C (mean of 277 °C). W-type inclusions are less abundant than C-type and yield $T_{\text{m-ice}}$ values between −3.7 and −0.5 °C (mean of −2.2 °C), corresponding to salinities of 0.9–6.0 wt.% NaCl eqv. (mean of 3.6 wt.% NaCl eqv.) and a ρ_{total} of 0.69–0.91 g/cm³ (mean of 0.82 g/cm³). These inclusions finally homogenize into the liquid or vapor phases (due to the volume percentage of vapor H₂O) with a temperature

of 190–349 °C, clustering at 200–260 °C (mean of 249 °C). Occurring in very few numbers, the PC-type inclusions are generally observed coexisting with C-type inclusions. Their T_{m-CO_2} values range from −61.5 to −57.2 °C (mean of −59.0 °C; Figure 9A), indicating CH₄ and/or N₂ in the CO₂ phases as additional gas species. The T_{h-CO_2} (to liquid phase) values are between 12.3 °C and 19.0 °C (mean of 16.1 °C; Figure 9C) with a calculated ρ_{CO_2} of 0.80–0.86 g/cm³ (mean of 0.82 g/cm³).

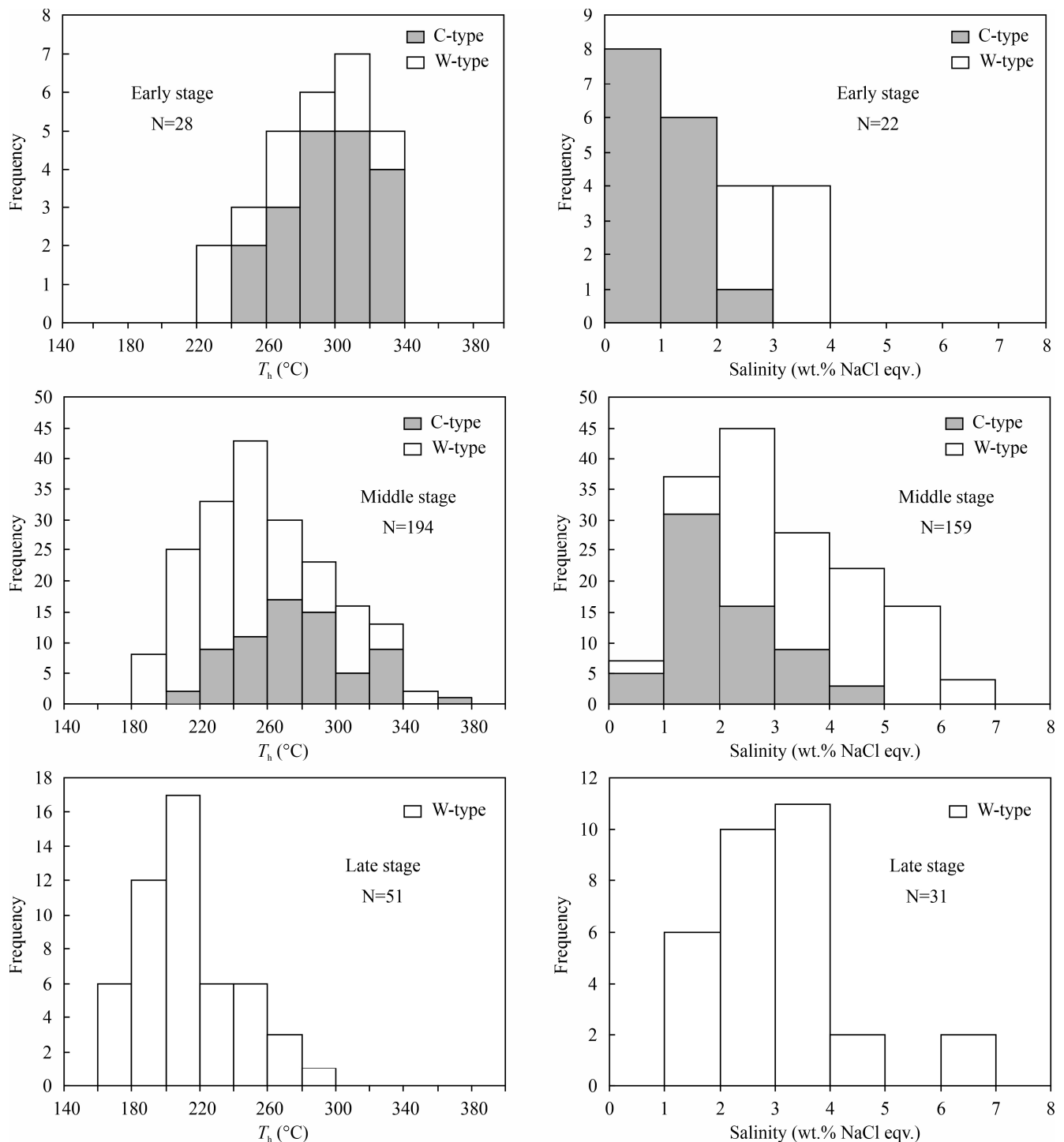


Figure 8. Histograms of total homogenization temperatures (T_h) and salinities of C- and W-type FIs in the Nanmingshui gold deposit.

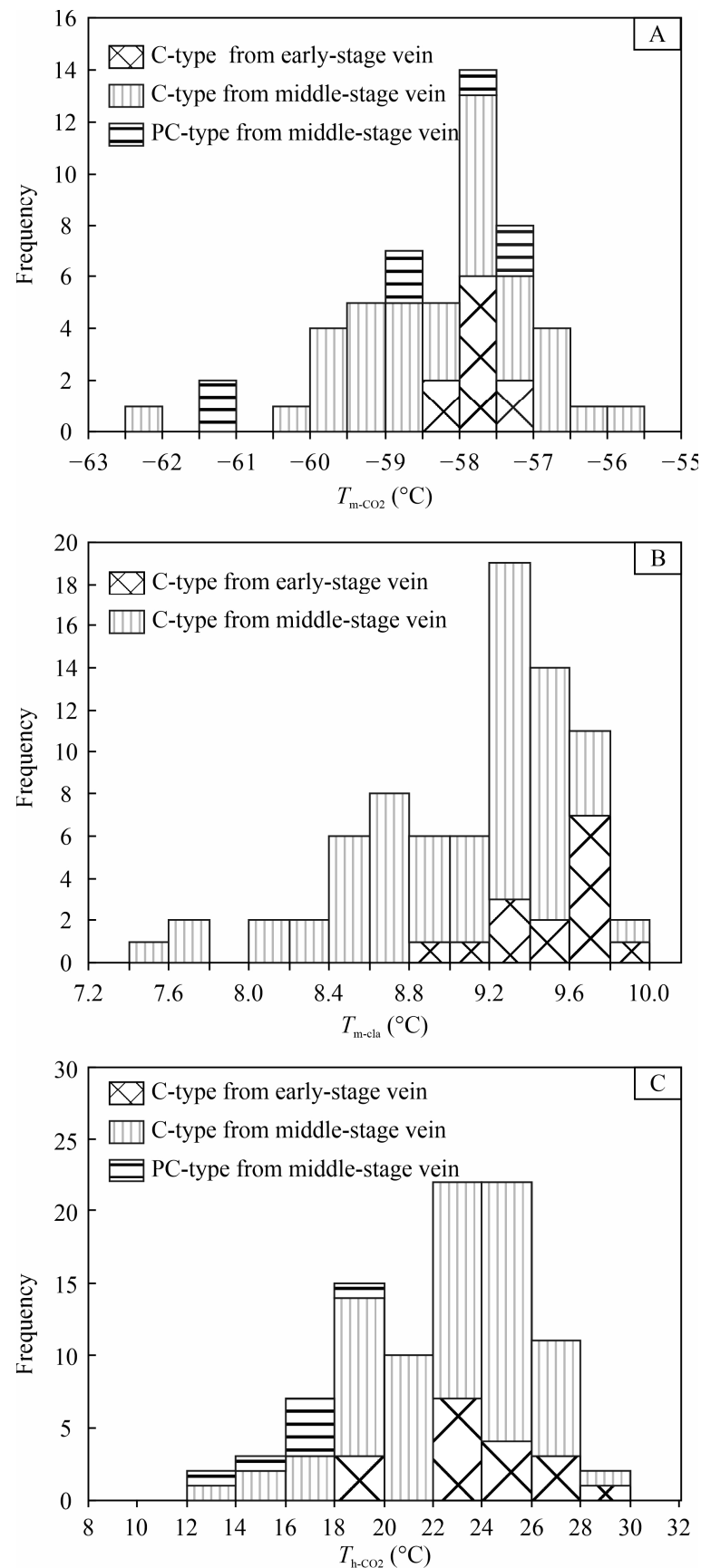


Figure 9. T_{m-CO_2} (A), T_{m-cla} (B), and T_{h-CO_2} (C) histograms for C- and PC-type FIs in the Nanmingshui gold deposit.

Late stage: Only the W-type inclusions were observed in late-stage quartz crystals. The T_{m-ice} values, ranging from -4.3 to -0.8 °C (mean of -1.8 °C), are indicative of a narrow salinity range of 1.4–6.9 wt.% NaCl eqv. (mean of 3.0 wt.% NaCl eqv.). The W-type FIs are all homogenized into the liquid phase at temperatures of 172–287 °C (mean of 213 °C) with the majority clustering at 180–220 °C. The calculated ρ_{total} values range from 0.79 to 0.95 g/cm³ (mean of 0.88 g/cm³).

5.2.3. Metallogenic Pressure and Depth

C-type FIs are common in the gold-bearing quartz veins of the early and middle stages. The ore-forming fluids at Nanmingshui are approximately medium–high-temperature, low-salinity (<7.0 wt.% NaCl eqv.), and CO₂-rich-H₂O-NaCl $\pm$ CH₄ $\pm$ N₂ systems. Therefore, we chose C-type FIs to estimate trapping pressure by using the Flnor program for the CO₂-H₂O-NaCl system [53]. The results are shown in Figure 10. Based on the microthermometric data and estimated volume fractions of the CO₂ phase, the calculated trapping pressures of the C-type inclusions are 208–367 MPa in the early stage and 206–392 MPa in the middle stage, with the majority clustering at 280–340 MPa and 220–310 MPa (Figure 10), respectively. Given 2.7 g/cm³ as an average density of the upper crust rocks, the metallogenic depths of the Nanmingshui gold deposit are estimated to be 10–13 km in the early stage and 8–11 km in the middle stage, assuming lithostatic conditions. Because Au mineralization mainly occurred in the middle stage, it can be concluded that the Nanmingshui gold deposit was formed at depth of ca. 8–11 km. These paleodepths are nearly consistent with the brittle–ductile transition zone, and are the favored depths (typically 5–18 km) of the most orogenic gold deposits in the world [3,62].

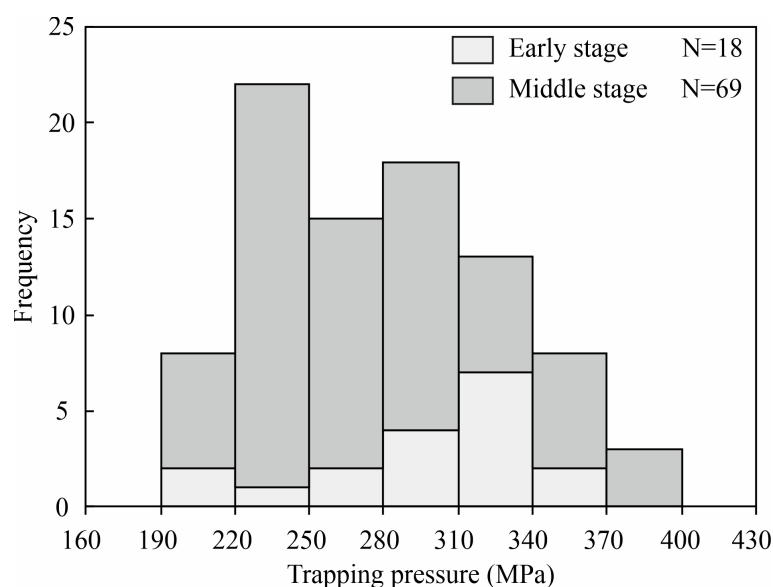


Figure 10. Histograms of trapping pressures of C-type FIs from the Nanmingshui gold deposit.

When neglecting the tectonic overpressure, the gold orebodies at Nanmingshui experienced a minimum 3 km uplift from the early to middle stages, accompanied by a simultaneous reduction in trapping pressures of approximately 30–60 MPa. This phenomenon is common in orogenic deposits, and can be interpreted as the promotion of seismic activity related to uplift and exhumation during orogenic processes [49,63].

5.2.4. Laser Raman Spectroscopy

Representative FIs were measured using Raman spectroscopy to reveal their gas compositions. The analysis of C-type (including type Ia and Ib) inclusions from early- and middle-stage quartz shows that the vapor or liquid CO₂ phases are dominated by CO₂, but contain minor amounts of CH₄ and/or N₂ (Figure 11A–D), which are consistent with the

T_{m-CO_2} being lower than $-56.6\text{ }^{\circ}\text{C}$ in the microthermometric process. Although no CO_2 phase can be observed during the cooling–heating runs, the vapor bubbles of W-type FIs in middle-stage quartz still contain minor amounts of additional CO_2 and CH_4 other than H_2O (Figure 11E). However, the existence of CO_2 in late-stage W-type inclusions was not detected by either the microthermometric measurement or the laser Raman spectroscopic analysis (Figure 11F), implying that CO_2 -based gas loss or phase separation occurred during the evolution of ore-forming fluid systems from CO_2 -rich aqueous solution in the early and middle stages to CO_2 -poor aqueous solution in the late stage. The petrographic evidence of PC-type inclusions coexisting with W-type inclusions can also strongly support this fact (Figure 7A,B).

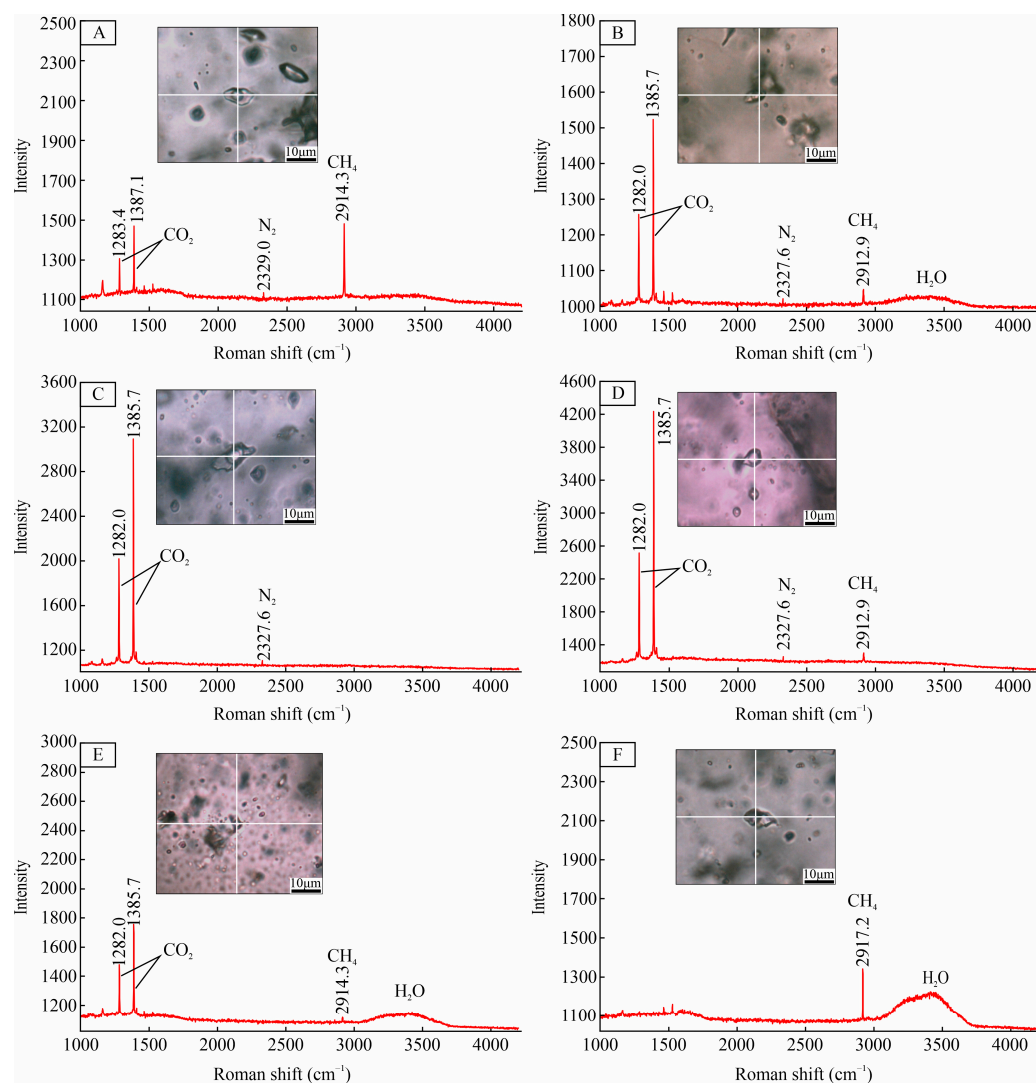


Figure 11. Representative Raman spectra of FIs in the Nanmingshui gold deposit. (A) Spectrum for liquid CO_2 phase of two-phase C-type inclusion in early-stage quartz, showing variable contents of CH_4 and N_2 , in addition to CO_2 ; (B) spectrum for liquid CO_2 phase of three-phase C-type inclusion in middle-stage quartz, containing minor amounts of N_2 , CH_4 , and H_2O , in addition to CO_2 ; (C) spectrum for three-phase C-type inclusion in middle-stage quartz, showing minor contents of N_2 in vapor CO_2 ; (D) spectrum for liquid CO_2 phase of CO_2 -rich inclusion in middle-stage quartz, containing variable N_2 and CH_4 , in addition to CO_2 ; (E) spectrum for vapor bubbles of W-type inclusion in middle-stage quartz, containing variable CO_2 and CH_4 ; (F) spectrum for vapor bubbles of W-type inclusion in late-stage quartz, containing variable CH_4 .

5.3. H-O Isotopic Compositions

The $\delta^{18}\text{O}$ values of the middle-stage auriferous quartz show restricted variation between 13.3 and 19.7‰ with an average value of 14.9‰ (Table 3). Based on the equation of oxygen isotopic fractionation between quartz and water ($1000\ln\alpha_{\text{quartz-water}} = 3.38 \times 10^6 T^{-2} - 3.4$) [55], the calculated fluid $\delta^{18}\text{O}_{\text{water}}$ values at Nanmingshui vary from 1.8 to 10.9‰ (mean of 6.1‰). Except for sample L1506, almost all the $\delta^{18}\text{O}_{\text{water}}$ and δD values (−99.0 to −62.9‰) of ore-forming fluids in the deposit are consistent with those of gold deposits (Jinshuiquan, Shuangquan, Sujiquandong, etc.) in the KGB ($\delta^{18}\text{O}_{\text{water}} = 4\text{--}12\text{‰}$, $\delta\text{D} = -100$ to -60‰) [26,31,64].

Table 3. H-O isotopic compositions of auriferous quartz from the Nanmingshui gold deposit (‰).

Sample No.	Mineral	$\delta\text{D}_{\text{water}}$	$\delta^{18}\text{O}_{\text{mineral}}$	T (°C)	$\delta^{18}\text{O}_{\text{water}}$	Reference
L1506	Quartz	−80.1	11.6	233	1.8	This study
L15114	Quartz	−68.7	14.0	261	5.5	
L15197	Quartz	−70.7	13.5	237	3.9	
NMS4-29	Quartz	−95.0	14.1	269	6.0	[26]
NMS4-30	Quartz	−92.0	19.0	269	10.9	
NMS7-6	Quartz	−82.0	14.8	253	6.0	
NMS7-7	Quartz	−99.0	19.7	253	10.9	[31]
SQD-84	Quartz	−99.0	13.3	256	4.6	
6N-53	Quartz	−62.9	13.9	255	5.2	[64]
Average		−83.3	14.9		6.1	

Note: T —average homogenization temperatures of fluid inclusions for each sample.

5.4. Zircon U-Pb Geochronology

The LA-ICP-MS analytical results of U-Pb dating and REE concentrations for 30 zircon grains separated from the No. 3 auriferous quartz–tourmaline vein are listed in Tables S1 and S2 (see the Supplementary Materials), and illustrated in Figures 12 and 13. According to the crystal morphology, internal structures, and dating results, two distinct types of zircons are recognized.

Type-1 zircons are generally beige-to-yellowish in color and rounded-to-subrounded in shape, and most are euhedral-to-subhedral crystals with diameters of 40–110 μm and aspect ratios of 1:1–3:1. More significantly, zircon crystals usually have bright CL responses and exhibit oscillatory zoning (Figure 12A), similar to igneous zircons crystallized during a single petrogenetic event [65]. The Th and U contents of type-1 zircons vary between 28–504 ppm and 48–840 ppm, respectively, with Th/U ratios of 0.13–1.17 (mostly >0.4). Their chondrite-normalized REE patterns from La to Lu are characterized by heavy (H) REE enrichment ($(\text{Lu}/\text{Sm})_{\text{N}} = 47\text{--}433$) and light (L) REE depletion ($(\text{Sm}/\text{La})_{\text{N}} = 18\text{--}1572$) with pronounced positive Ce anomalies ($\delta\text{Ce} = 4.77\text{--}182.43$) and negative Eu anomalies ($\delta\text{Eu} = 0.03\text{--}0.65$; Figure 13A), which are typical for magmatic zircon [66]. Furthermore, all data points of the type-1 zircons are plotted within or near the magmatic field in Figure 13B. The LA-ICP-MS U-Pb ages of 28 type-1 zircons fall into two populations (Figure 12A,B). One cluster of 13 analyzed points yields $^{206}\text{Pb}/^{238}\text{U}$ ages ranging from 426 to 410 Ma with a weighted mean of 416.6 ± 3.7 Ma (MSWD = 0.79, Figure 12C). The other cluster of nine analyzed points yields $^{206}\text{Pb}/^{238}\text{U}$ ages ranging from 404 to 385 Ma with a weighted mean of 396.3 ± 4.2 Ma (MSWD = 1.13, Figure 12D). These two weighted mean ages can be interpreted as xenocrysts incorporated from the Kalamaili ophiolite [44]. In addition, three analyses have a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 500 ± 11 Ma (MSWD = 0.56, Figure 12B), which is consistent with the early SHRIMP zircon U-Pb dates for plagiogranite (497 ± 12 Ma) from the KOB. Two zircon grains yield a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 962 ± 19 Ma (MSWD = 0.34, Figure 12A). One grain gives a Neoproterozoic $^{207}\text{Pb}/^{206}\text{Pb}$ age of 2611 ± 59 Ma (Figure 12A), suggesting that it is a zircon xenocryst from the hidden Archean crust (ca. 3.8–2.55 Ga) beneath the Junggar terrane [67].

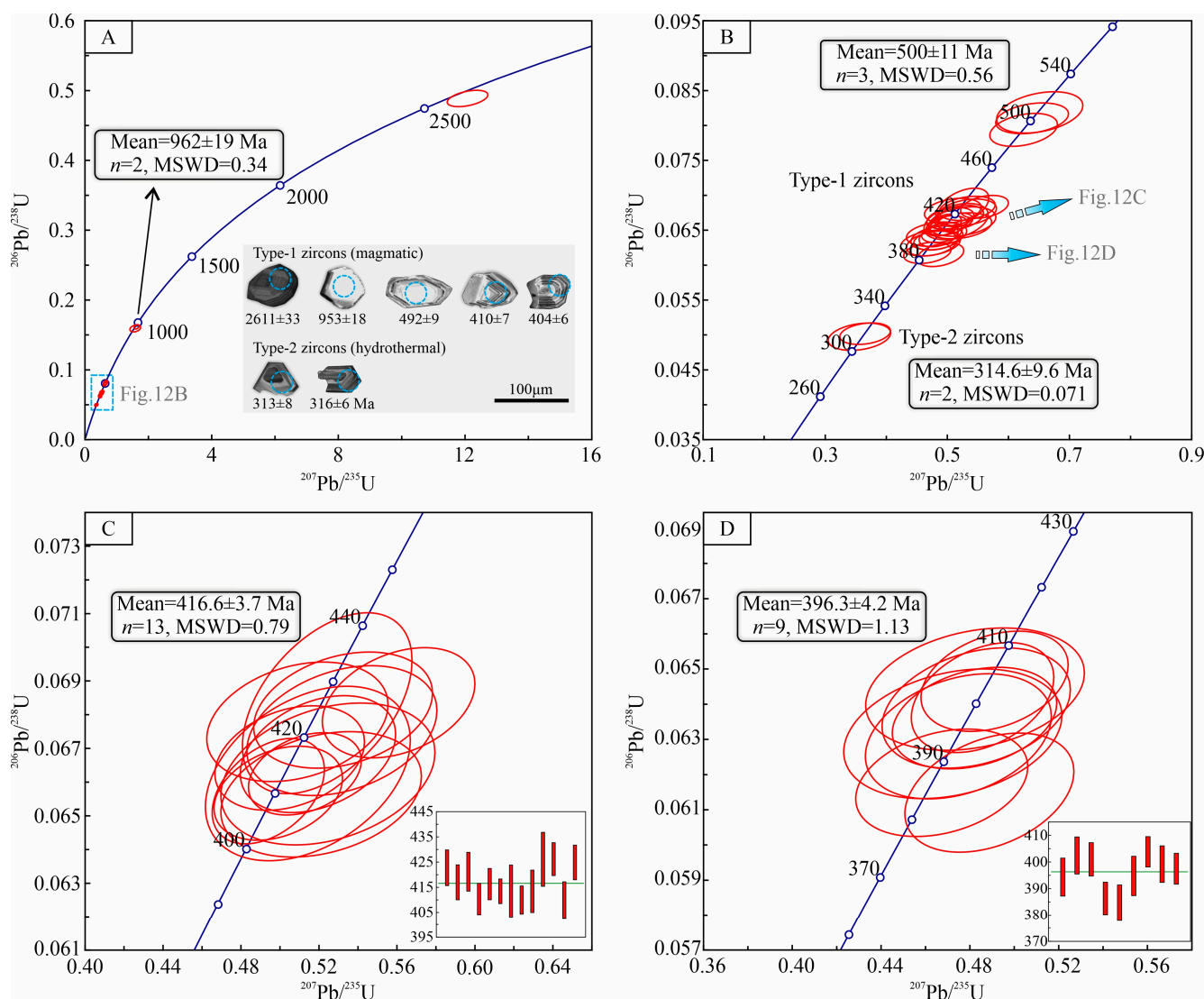


Figure 12. Representative CL images, U-Pb Concordia diagrams, and weighted mean ages of magmatic and hydrothermal zircons from the auriferous quartz–tourmaline vein in the Nanmingshui gold deposit. (A,B) U-Pb Concordia diagrams for all analyzed zircons; (C,D) U-Pb Concordia diagrams and weighted mean ages for type-1 zircons (magmatic).

Two grains of type-2 zircon are smaller in size, with diameters of 58–62 μm and aspect ratios of 1:1–3:2. In the CL images, both have no or extremely low CL responses and show internally structureless or ambiguous oscillatory zoning (Figure 12A). Type-2 zircons have relatively higher Th contents (100–272 ppm, mean of 186 ppm) and lower U contents (171–248 ppm, mean of 210 ppm) than type-1 zircons (mean of 129 ppm Th and 304 ppm U), with Th/U ratios of 0.58–1.09. The lower total REE ($\Sigma\text{REE} = 827\text{--}1177$ ppm vs. 415–4142 ppm for type-1 zircons) and HREE concentrations (HREE = 753–989 ppm vs. 405–4078 ppm for igneous zircons) and higher LREE concentrations (LREE = 74–188 ppm vs. 6–64 ppm for type-1 ones) of type-2 zircons, combined with their flatter or less steep chondrite-normalized REE patterns ($(\text{Sm}/\text{La})_{\text{N}} = 0.62\text{--}0.92$ and $\delta\text{Ce} = 2.37\text{--}2.85$; Figure 13A), are obviously distinct from those of type-1 magmatic zircons. In particular, in the $(\text{Sm}/\text{La})_{\text{N}}$ versus La discriminant diagram [68,69], type-2 zircons are plotted around the hydrothermal zircon field (Figure 13B), suggesting a hydrothermal origin. Two hydrothermal zircons yield $^{206}\text{Pb}/^{238}\text{U}$ ages that vary from 313 to 316 Ma with a Late Carboniferous weighted mean age of 314.6 ± 9.6 Ma (MSWD = 0.071, Figure 12B).

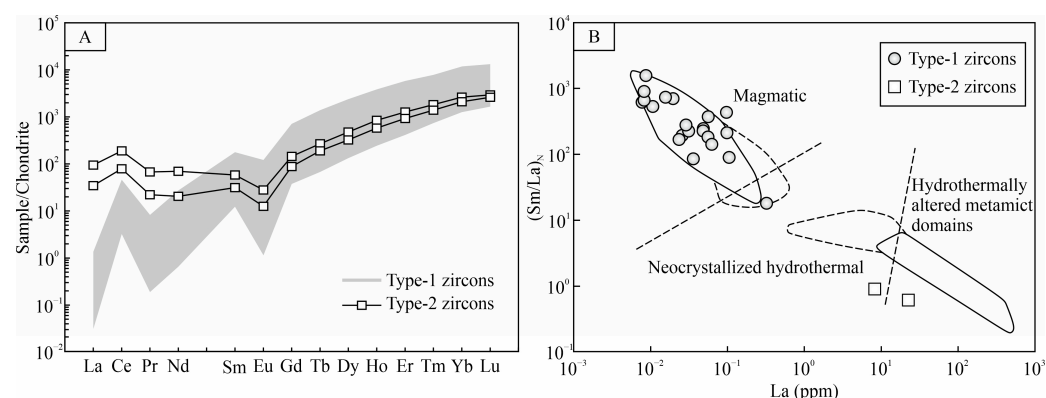


Figure 13. (A) Chondrite-normalized REE patterns (normalization values from [70]) and (B) discriminant diagrams of $(\text{Sm/La})_N$ versus La for zircons from the auriferous quartz–tourmaline vein in the Nanmingshui gold deposit (after [68,69]).

6. Discussion

6.1. Gold Occurrences in Pyrite and Arsenopyrite

The presence of gold in natural ores, generally occurring as discrete gold minerals (native gold, Au–Ag tellurides, aurostibite, maldonite, auricupride, etc.) and submicroscopic or invisible (so-called refractory) gold [71,72], is a potential indicator for identifying Au-bearing deposit types [73]. It is also crucial for the recovery of gold during mineral processing [74]. In a great variety of gold deposit types (orogenic, Carlin, epithermal, intrusion-related, etc.), either native gold or invisible gold is principally hosted by (arsenian) pyrite and arsenopyrite. In particular, the concentrations of refractory gold can vary from a few tens of ppb to more than 1.0 wt.% of its hosts [61,75,76].

In the Nanmingshui gold deposit, four kinds of occurrence states for native gold (sizes of 1–60 μm) are observed in high-grade ores, including microscopic inclusions in arsenopyrite (60%, Figure 14A), intergranular grains in contact with the boundary of pyrite and arsenopyrite (30%, Figure 14B), elongated fissure-filled grains within the pseudomorphs of hematite after pyrite (8%, Figure 14C), and less common disseminated or isolated grains in quartz (2%, Figure 14D). The high gold fineness (941–944) and Hg contents (2.42–2.56 wt.%, mean of 2.50 wt.%) of native gold from the Nanmingshui gold deposit, together with gold textures, are almost consistent with the orogenic gold deposits [62,73]. On the basis of the EPMA data in this study (Table 1), both arsenian pyrite₂ and arsenopyrite incorporate minor amounts of refractory gold, with Au values ranging from bdl to 0.08 wt.% (mean of 0.02 wt.%, $n = 10$) and bdl to 0.01 wt.% (mean of 0.004 wt.%, $n = 8$), respectively. The results of EDS mapping reveal that the gold-hosted minerals have homogeneous distributions of gold without any Au-rich points. Combined with the Au/As molar ratios of 0–0.015 (mostly 0–0.004) in arsenian pyrite and arsenopyrite falling below the maximum solid-solution Au lines (Figure 15) [75,77], it can be inferred that invisible gold may occur as solid solutions (Au^+) in the crystal lattice [78] rather than as discrete microparticles and nanoparticles (Au^0) [79].

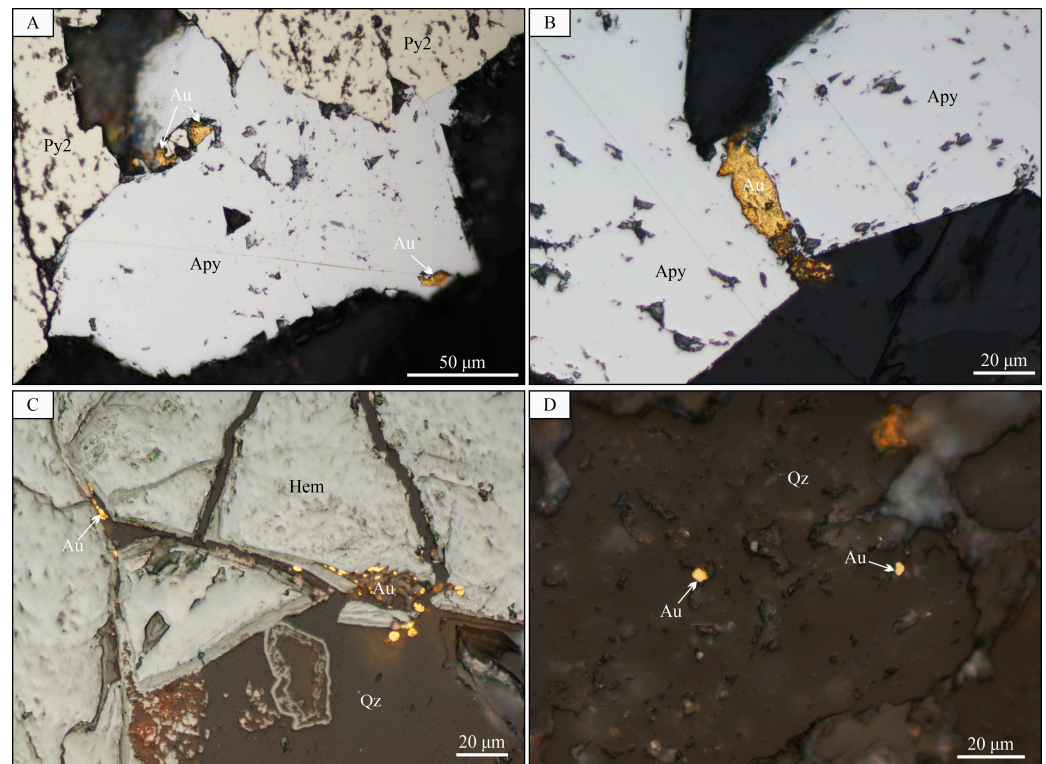


Figure 14. Microphotographs of native gold in the Nanmingshui gold deposit. (A) Native gold occurring in arsenopyrite as anhedral inclusions (reflected light); (B) native gold occurring as intergranular grains in contact with the margin of arsenopyrite (reflected light); (C) elongated gold filling in fissures within the pseudomorph of hematite after pyrite (reflected light); (D) native gold occurring in quartz as isolated grains (reflected light). For mineral abbreviations, see Figure 4.

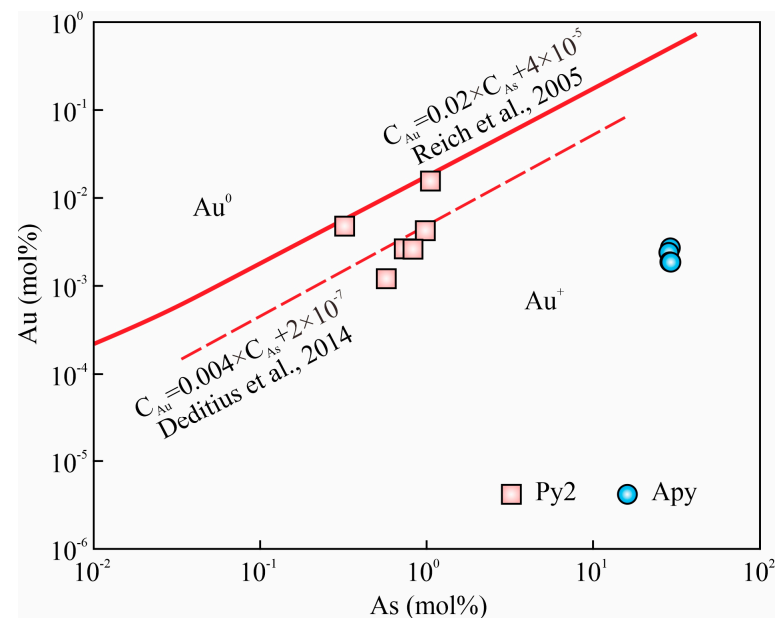


Figure 15. Au-As plot showing EPMA analyses of arsenian pyrite and arsenopyrite from the Nanmingshui gold deposit. Solid line represents the Au saturation line for Carlin-type gold deposits [77], and dashed line represents that for orogenic gold deposits [75]. For mineral abbreviations, see Figure 3.

6.2. Nature and Evolution of Ore-forming Fluids

The measured $\delta^{18}\text{O}$ values of auriferous quartz from the Nanmingshui gold deposit show restricted variations between 13.3 and 19.7‰ (mean of 14.9‰; Table 3), which are typical of orogenic gold deposits from the Neoproterozoic to Cenozoic ($\delta^{18}\text{O} = 10\text{--}18\text{‰}$) [80–82]. Except for individual $\delta^{18}\text{O}_{\text{water}}$ values, the majority fall into the range of most lode gold deposits ($\delta^{18}\text{O}_{\text{water}} = 5\text{--}11\text{‰}$) [12,13,83]. The δD values range from -99.0 to -62.9‰ with an average of -83.3‰ and overlap with those of the Juneau gold belts, Alaska (Figure 16) [84]. In Figure 16, all values are plotted away from the meteoric water line and below or in the metamorphic and primary magmatic H_2O boxes, suggesting that the metallogenetic fluids are likely to be derived from metamorphic or magmatic H_2O rather than meteoric water. Furthermore, the $\delta^{18}\text{O}_{\text{water}}$ values of samples NMS4-30 and NMS7-7 are both 10.9‰ (Table 3), which are obviously higher than the maximum $\delta^{18}\text{O}$ value (9‰) of magmatic water [85] and the $\delta^{18}\text{O}$ values (5.4–10.35‰) of A-type granites in the north of the KOB [86]. Considering the geological fact that there are no reported granitic intrusions at the mining area and the fluid P - T - X conditions (Table 2), the ore-forming fluids at Nanmingshui probably originated from the metamorphic devolatilization of $\delta^{18}\text{O}$ -enriched rocks instead of being granitic or meteoric H_2O in origin.

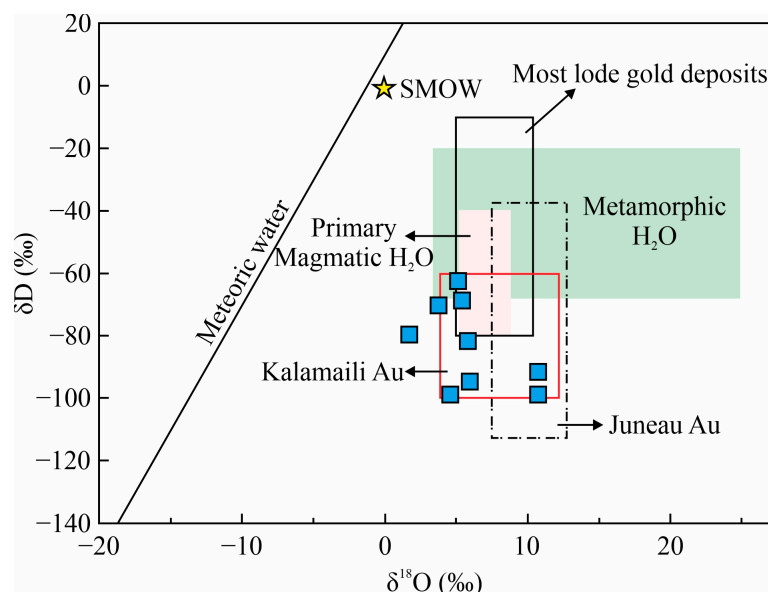


Figure 16. Calculated δD and $\delta^{18}\text{O}$ of the ore-forming fluids at Nanmingshui. Fields for primary magmatic and metamorphic waters are cited from reference [87], and domains for other deposits are given in the text.

In cases where gold particles in or around the FIs and temporal relationships between the ore and gangue minerals are not observed, relying on the inclusion data to constrain the geological environment or metallogenetic processes remains inconclusive [88,89]. However, fluid inclusions, at least the primary FIs in the earliest-stage minerals, are potential indicators for the genesis of hydrothermal mineral systems [90]. Hydrothermal quartz at the Nanmingshui deposit generally coexists with gold-bearing minerals (Figure 14) and contains various types of FIs, which can be used to trace the nature and evolution of ore-forming fluids.

As shown in Figure 8, the T_h values of FIs decrease from 220–339 °C (peaking at 260–320 °C) during the early stage to 190–361 °C (peaking at 220–280 °C) during middle stage, and to 172–287 °C (peaking at 180–220 °C) during late stage. Meanwhile, the salinities of the FIs increase slightly from 0.4–3.7 wt.% NaCl eqv. in the early stage to 0.4–6.0 wt.% NaCl eqv. in the middle stage, and to 1.4–6.9 wt.% NaCl eqv. in the late stage. The occurrence of numerous C- and W-type FIs in the early-stage quartz indicates that the initial fluids are

most likely low-salinity and carbonic–aqueous. Furthermore, the coexistence of the C-, W-, and PC-type FIs with variable salinities and divergent homogenization behaviors implies that fluid immiscibility occurred in the early and middle stages, whereas the late-stage quartz only contains W-type inclusions without any CO₂ detected, suggesting a CO₂-poor aqueous solution. Thus, from the early to late stages, it can be concluded that the ore fluids evolved from CO₂-rich to CO₂-poor solutions through fluid immiscibility and CO₂ escape.

In conclusion, the ore-forming fluids at the Nanmingshui deposit are characterized by medium–high-temperature, low-salinity (<7.0 wt.% NaCl eqv.), and CO₂-rich-H₂O-NaCl ± CH₄ ± N₂ systems with metamorphic water at the origin, similar to those of the orogenic gold deposits around the world [1,3,62].

6.3. Fluid Immiscibility and Gold Deposition

Fluid immiscibility is a process frequently invoked as the cause for gold deposition in many mesothermal lode gold deposits [89,91]. Most mesothermal veins typically formed below the levels at which water could boil, and the presence of CO₂ in FIs allowed fluid immiscibility to occur at much greater depths [92]. Following the criteria outlined by Ramboz et al. [93], we found that fluid immiscibility can be a crucial mechanism for gold deposition in the Nanmingshui gold deposit. Our evidence is as follows: (1) The PC-type and/or C-type Ib, and W-type FIs, in many cases, coexist in the same clusters or trails of the same quartz crystal (Figure 7A,B,G). The petrographic, microthermometric, and laser Raman data collected from these inclusions imply that they are accidentally trapped in two end-member fluids (a CO₂-rich fluid and a H₂O-rich aqueous solution), resulting from the unmixing of a low-salinity H₂O-CO₂ parent fluid [94]. (2) The coexistence of these three-types of inclusions (PC-type, C-type Ib, and W-type) with rare C-type Ia inclusions, containing highly variable X_{CO2} concentrations (0.07–0.58; Table 2), can be explained by the heterogeneous entrapment of the carbonic and aqueous end-member fluids [8,91]. Heterogeneous trapping represents simple but solid evidence for fluid immiscibility. (3) The T_h values for C-type inclusions are commonly higher than those for cogenetic W-type inclusions (Figure 7, Figure 17). This phenomenon may be due to the heterogeneous trapping of a small amount of H₂O-rich fluid within CO₂-rich inclusions [88,95], which is also consistent with fluid immiscibility [96]. (4) Compared with C-type inclusions in the same stage, W-type FIs tend to have higher salinities (Figure 17), as the salt is preferentially fractionated into the aqueous phase rather than the CO₂-rich phase [92]. The relatively high salinity of H₂O-rich fluid can be produced via unmixing of the low-salinity H₂O-CO₂ parent fluid. (5) Despite no aqueous phases being observed in PC-type inclusions at room temperature, the small size of these inclusions may contain microscopically undetectable H₂O (up to 10–20 vol.%) [97,98], implying that the occurrence of PC-type FIs may be due to phase separation from a CO₂-H₂O-NaCl fluid.

The fluid immiscibility at Nanmingshui is likely to be induced by sudden drops in fluid pressure, rather than the gradual cooling of ore fluids. This process is strongly supported by the 30–60 MPa decreases in trapping pressure from the early to middle stages (Figure 10) and the partial overlapping of T_h values between each stage (Figure 17).

On the basis of previous experiments on Au⁺ complexing in aqueous sulfide solutions [99,100], gold was probably transported as a bisulfide complex Au(HS)₂[−] in lode-gold-only deposits like Nanmingshui [101]. Thus, the gold concentrations can be related to those of the sulfide species via the following: Au + H₂S + HS[−] = Au(HS)₂[−] + 0.5H₂, H₂S = HS[−] + H⁺. Two possible mechanisms can promote the deposition of gold at Nanmingshui by breaking down the bisulfide complexes. First, phase separation in the immiscible fluids can strongly fractionate H₂S into the vapor phase, resulting in a pH increase in the liquid [27]. Second, the abundant CO₂ and other additional volatiles (such as CH₄ and N₂) may play a critical role [102]. CO₂ occurs as a pH buffer to maintain elevated concentrations of gold in ore fluids, and can be removed via phase separation, leading to the destruction of CO₂ buffering pH [103]. Moreover, the existence of CH₄ and N₂ can push the solvus to higher P-T conditions, making phase separation easier [104].

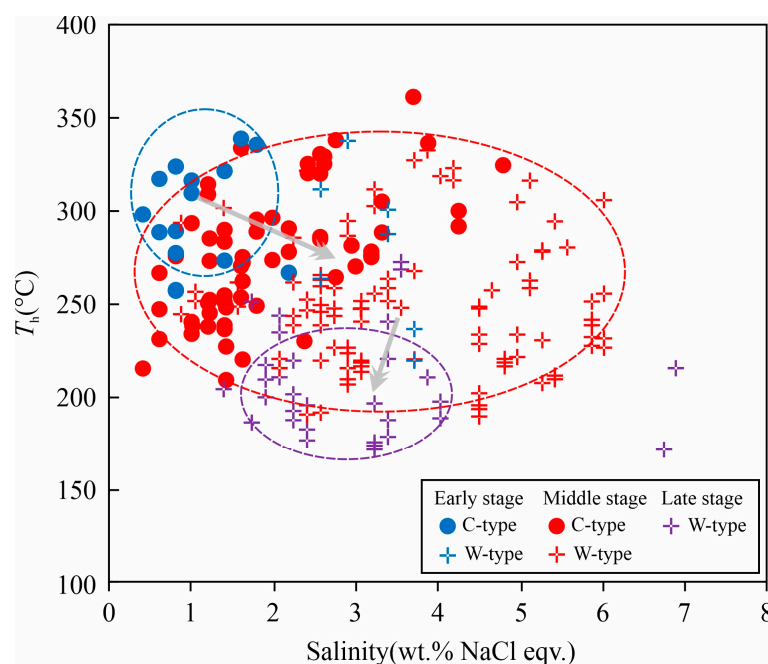


Figure 17. Plot of T_h vs. salinity for fluid inclusions in quartz from the Nanmingshui gold deposit.

6.4. Timing of Gold Mineralization

Zircon (ZrSiO_4) is commonly considered to be an ideal mineral for geochronological studies, as a result of its stable physicochemical properties and high closure temperature (greater than 900 °C) for the U-Th-Pb isotopic system [105]. Hydrothermal zircon U-Pb geochronology has been widely used as a direct dating method to determine the metallogenic ages of distinct hydrothermal deposits, such as Archean massive sulfide deposits [106], orogenic Au [107–109], Fe skarn [110], Nb-Ta-U-REE [111–113], and intrusion-related W-Sn-Mo-Bi-Au deposits [114,115]. It has been demonstrated that the crystallization and growth of hydrothermal zircon are common in low-temperature environments, with P - T conditions of 260–380 °C and 7–200 MPa [107,108,115–118].

The P - T conditions above are similar to the ranges of the main ore fluid (220–280 °C and 220–310 MPa) in the Nanmingshui gold deposit, implying that hydrothermal zircon can crystallize from this mesothermal fluid. Indeed, two zircon grains from the auriferous quartz–tourmaline vein yield $^{206}\text{Pb}/^{238}\text{U}$ ages of 313–316 Ma, with a weighted mean age of 314.6 ± 9.6 Ma. Their CL images, U-Th-Pb concentrations, and REE compositions are more consistent with those of hydrothermal zircons from the Jack Hills, Australia, than those of magmatic zircons captured from the Archean crust and Kalamaili ophiolite (Table S1; Figure 13) [68]. Thus, the Late Carboniferous age of ca. 315 Ma can be recognized as the period of gold mineralization at Nanmingshui.

Besides the U-Pb dating results of hydrothermal zircon, three geological constrains may contribute to determining the mineralization age of the gold deposit: (1) The gold-bearing quartz veins are hosted in the rocks of the Upper Carboniferous Jiangbasitao Formation, whose zircon U-Pb ages are 339–336 Ma, giving a lower limit (336 Ma) of gold mineralization [119]. Both auriferous veins and wall-rocks were strongly deformed via foliation and mylonitization, while the A-type granitic intrusions (311–283 Ma) along the north of the KOB were not subjected to regional deformation and metamorphism [26]. Thus, the metallogenic age of the Nanmingshui gold deposit is reasonably restrained at 336–311 Ma. (2) Taking the latest research together, after the closure (ca. 340–330 Ma) of the Kalamaili Ocean and the collision (ca. 330–320 Ma) between the Jiangjunmiao accretionary complex and Yemaquan arc, a tectonic transition from syn-collisional compression to post-collisional extension (320–300 Ma) occurred during the Late Carboniferous [30,120]. This transition of tectono-thermal regimes is conducive to driving the fluid in deep and forming the hy-

drothermal deposits [121]. (3) Many gold deposits in the KGB were formed between 318 and 310 Ma, such as the Qingshui No. 48 (quartz Rb-Sr isochron age of 311 ± 46 Ma) [122], Huangyangshanxi (zircon U-Pb ages of 318–310 Ma) [123], and Jinshuiquan (hydrothermal zircon U-Pb age of 314.9 ± 3.2 Ma) [124] gold deposits, indicating that at least an essential hydrothermal event of gold mineralization occurred during the Late Carboniferous.

These facts correspond well with the hydrothermal zircon U-Pb ages in this study. Therefore, it is reasonable to deduce that the Nanmingshui gold deposit was formed in the Late Carboniferous (ca. 315 Ma) rather than Early Carboniferous (337.5 ± 3.9 Ma) [32], which marked a transitional setting from the syn-collision between the Jiangjunmiao accretionary complex and Yemaquan arc to post-collision in the Kalamaili area, East Junggar.

6.5. Ore Genetic Type

Many of the geological and geochemical features exhibited by Nanmingshui are similar to those of typical orogenic gold deposits [7,8,62,109,125]: (1) The deposit was formed in the Late Carboniferous, with an age of ca. 315 Ma, which was in a transitional period after the collision between the Jiangjunmiao accretionary complex and the Yemaquan arc in the East Junggar Orogen. (2) The gold-bearing veins, mainly controlled by the NW- to NWW-trending brittle–ductile faults, are hosted in the sub-greenschist facies rocks of the Lower Carboniferous Jiangbasitao Formation. (3) Metallic minerals in ores consist of arsenopyrite and (arsenian) pyrite and minor pyrrhotite, chalcopyrite, sphalerite, galena, tetrahedrite, and native gold, with total contents < 5%. Most of the gold occurs as native gold in sulfides and quartz, with high gold fineness of 941–944. (4) Extensive wall-rock alteration and lateral zoning can be observed. The alteration types primarily consist of silicification, arsenopyritization, pyritization, sericitization, carbonatization, chloritization, and epidotization. (5) The main ore fluid belongs to a mesothermal (220–280 °C), low-salinity (<7.0 wt.% NaCl eqv.), and CO₂-rich-H₂O-NaCl $\pm$ CH₄ $\pm$ N₂ system, with calculated pressures of 220–310 MPa and estimated depths of 8–11 km. (6) The $\delta^{18}\text{O}_{\text{water}}$ (1.8–10.9‰) and δD values (−99.0 to −62.9‰) for the metallogenic fluids were probably derived from the metamorphic H₂O. (7) Fluid immiscibility is one of the most important mechanisms for gold deposition.

Taking all of the above together, here, we propose that the Nanmingshui gold deposit can be classed as an orogenic gold deposit as defined by Groves et al. [3].

7. Conclusions

In this paper, a systemic study of mineralogy, geochemistry, and geochronology was conducted, aiming to constrain the gold mineralization and genesis of the Nanmingshui gold deposit in the KGB, Xinjiang, NW China. Our research draws the following conclusions:

(1) Three metallogenic stages are recognized at Nanmingshui, marked by the mineral assemblages of early-stage quartz–pyrite–minor native gold veins, middle-stage quartz–tourmaline–arsenopyrite–pyrite–gold–polymetallic sulfide veins, and late-stage quartz–calcite veinlets. Gold in ores mainly occurs as native gold with high fineness (941–944) in sulfides and quartz, and some as solid solutions (Au⁺) in the lattice of pyrite and arsenopyrite.

(2) The ore-forming fluids at Nanmingshui are characterized by medium–high-temperature, low-salinity, medium-density, and CO₂-rich-H₂O-NaCl $\pm$ CH₄ $\pm$ N₂ systems, probably derived from metamorphic water. Fluid immiscibility is a key mechanism for gold precipitation.

(3) The Nanmingshui deposit is a typical mesozonal (metallogenic depths of ca. 8–11 km) orogenic gold deposit in the KGB. It was formed in a Late Carboniferous tectonic transition from syn-collision between the Jiangjunmiao accretionary complex and Yemaquan arc to post-collision in the East Junggar Orogen.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min13101296/s1>, Table S1: LA-ICP-MS U-Pb data of zircons from the auriferous quartz–tourmaline vein in the Nanmingshui gold deposit; Table S2: REE compositions (ppm) of zircons from the auriferous quartz–tourmaline vein in the Nanmingshui gold deposit.

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References

- Groves, D.I.; Santosh, M.; Deng, J.; Wang, Q.F.; Yang, L.Q.; Zhang, L. A holistic model for the origin of orogenic gold deposits and its implications for exploration. *Miner. Depos.* **2020**, *55*, 275–292. [\[CrossRef\]](#)
- Hou, Z.Q.; Wang, Q.F.; Zhang, H.J.; Yu, N.; Wang, R.; Groves, D.I.; Zheng, Y.C.; Han, S.C.; Gao, L.; Yang, L. Lithosphere architecture characterized by crust-mantle decoupling controls the formation of orogenic gold deposits. *Natl. Sci. Rev.* **2023**, *10*, nwac257. [\[CrossRef\]](#) [\[PubMed\]](#)
- Groves, D.I.; Goldfarb, R.J.; Gebre-Mariam, M.; Hagemann, S.G.; Robert, F. Orogenic gold deposits: A proposed classification in the context of their crustal distribution and relationship to other gold deposit types. *Ore Geol. Rev.* **1998**, *13*, 7–27. [\[CrossRef\]](#)
- Mueller, A.G.; Hagemann, S.G. A thematic issue dedicated to the giant Golden Mile Au-Te deposit, Kalgoorlie, Western Australia. *Miner. Depos.* **2020**, *55*, 597–600. [\[CrossRef\]](#)
- Chudasama, B.; Porwal, A.; Kreuzer, O.P.; Butera, K. Geology, geodynamics and orogenic gold prospectivity modelling of the Paleoproterozoic Kumasi Basin, Ghana, West Africa. *Ore Geol. Rev.* **2016**, *78*, 692–711. [\[CrossRef\]](#)
- White, A.J.R.; Waters, D.J.; Robb, L.J. Exhumation-driven devolatilization as a fluid source for orogenic gold mineralization at the Damang deposit, Ghana. *Econ. Geol.* **2015**, *110*, 1009–1025. [\[CrossRef\]](#)
- Lawrence, D.M.; Treloar, P.J.; Rankin, A.H.; Harbidge, P.; Holliday, J. The geology and mineralogy of the Loulo mining district, West Africa: Evidence for two distinct styles of orogenic gold mineralization. *Econ. Geol.* **2013**, *108*, 199–227. [\[CrossRef\]](#)
- Lawrence, D.M.; Treloar, P.J.; Rankin, A.H.; Boyce, A.; Harbidge, P. A fluid inclusion and stable isotope study at the Loulo Mining District, Mali, West Africa: Implications for multifluid sources in the generation of orogenic gold deposits. *Econ. Geol.* **2013**, *108*, 229–257. [\[CrossRef\]](#)
- Qiu, Y.M.; Groves, D.I.; McNaughton, N.J.; Wang, L.G.; Zhou, T.H. Nature, age, and tectonic setting of granitoid-hosted, orogenic gold deposits of the Jiaodong Peninsula, eastern North China craton, China. *Miner. Depos.* **2002**, *37*, 283–305. [\[CrossRef\]](#)
- Zhang, L.; Weinberg, R.F.; Yang, L.Q.; Groves, D.I.; Sai, S.X.; Matchan, E.; Phillips, D.; Kohn, B.P.; Miggins, D.P.; Liu, Y.; et al. Mesozoic orogenic gold mineralization in the Jiaodong Peninsula, China: A focused event at 120 ± 2 Ma during cooling of pregold granite intrusions. *Econ. Geol.* **2020**, *115*, 415–441. [\[CrossRef\]](#)
- Qiu, K.F.; Deng, J.; Laflamme, C.; Long, Z.Y.; Wan, R.Q.; Moynier, F.; Yu, H.C.; Zhang, J.Y.; Ding, Z.J.; Goldfarb, R. Giant Mesozoic gold ores derived from subducted oceanic slab and overlying sediments. *Geochim. Cosmochim. Acta* **2023**, *343*, 133–141. [\[CrossRef\]](#)
- McCuaig, T.C.; Kerrich, R. P-T-t deformation-fluid characteristics of lode gold deposits: Evidence from alteration systematics. *Ore Geol. Rev.* **1998**, *12*, 381–454. [\[CrossRef\]](#)
- Kerrich, R.; Goldfarb, R.J.; Groves, D.; Garwin, S.; Jia, Y.F. The characteristics, origins, and geodynamic settings of supergiant gold metallogenic provinces. *Sci. China Ser. D* **2000**, *43*, 1–68. [\[CrossRef\]](#)
- Goldfarb, R.J.; Groves, D.I.; Gardoll, S. Orogenic gold and geologic time: A global synthesis. *Ore Geol. Rev.* **2001**, *18*, 1–75. [\[CrossRef\]](#)
- Groves, D.I.; Santosh, M. The giant Jiaodong gold province: The key to a unified model for orogenic gold deposits? *Geosci. Front.* **2016**, *7*, 409–417. [\[CrossRef\]](#)
- Groves, D.I.; Santosh, M.; Goldfarb, R.J.; Zhang, L. Structural geometry of orogenic gold deposits: Implications for exploration of world-class and giant deposits. *Geosci. Front.* **2018**, *9*, 1163–1177. [\[CrossRef\]](#)
- Nesbitt, B.E. Gold deposit continuum: A genetic model for lode Au mineralization in the continental crust. *Geology* **1988**, *6*, 1044–1048. [\[CrossRef\]](#)
- Neumayr, P.; Walshe, J.; Hagemann, S.; Petersen, K.; Roache, A.; Frikken, P.; Horn, L.; Halley, S. Oxidized and reduced mineral assemblages in greenstone belt rocks of the St. Ives gold camp, Western Australia: Vectors to high-grade ore bodies in Archaean gold deposits? *Miner. Depos.* **2008**, *43*, 363–371. [\[CrossRef\]](#)

19. Helt, K.M.; Williams-Jones, A.E.; Clark, J.R.; Wing, B.A.; Wares, R.P. Constraints on the genesis of the Archean oxidized, intrusion-related Canadian Malartic gold deposit, Quebec, Canada. *Econ. Geol.* **2014**, *109*, 713–735. [\[CrossRef\]](#)
20. Goldfarb, R.J.; Groves, D.I. Orogenic gold: Common or evolving fluid and metal sources through time. *Lithos* **2015**, *233*, 2–26. [\[CrossRef\]](#)
21. Spence-Jones, C.P.; Jenkin, G.R.; Boyce, A.J.; Hill, N.J.; Sangster, C.J.S. Tellurium, magmatic fluids and orogenic gold: An early magmatic fluid pulse at Cononish gold deposit, Scotland. *Ore Geol. Rev.* **2018**, *102*, 894–905. [\[CrossRef\]](#)
22. Windley, B.F.; Alexeiev, D.; Xiao, W.J.; Kröner, A.; Badarch, G. Tectonic models for accretion of the Central Asian orogenic belt. *J. Geol. Soc. Lond.* **2007**, *164*, 31–47. [\[CrossRef\]](#)
23. Rui, Z.Y.; Goldfarb, R.J.; Qiu, Y.M.; Zhou, T.H.; Chen, R.Y.; Pirajno, F.; Yun, G. Paleozoic-early Mesozoic gold deposits of the Xinjiang Autonomous Region, northwestern China. *Miner. Depos.* **2002**, *37*, 393–418. [\[CrossRef\]](#)
24. Goldfarb, R.J.; Taylor, R.D.; Collins, G.S.; Goryachev, N.A.; Orlandini, O.F. Phanerozoic continental growth and gold metallogeny of Asia. *Gondwana Res.* **2014**, *25*, 48–102. [\[CrossRef\]](#)
25. Zheng, J.H.; Shen, P.; Feng, W.Y. Hydrothermal apatite record of ore-forming processes in the Hatu orogenic gold deposit, West Junggar, Northwest China. *Contrib. Mineral. Petrol.* **2022**, *177*, 27. [\[CrossRef\]](#)
26. Gu, X.X.; Zhang, Y.M.; Ge, Z.L.; Chen, W.Z.; Xu, J.C.; Huang, G.; Tao, W. The orogenic Au mineralization system and regional tectonic evolution in the Kalamaili area, East Junggar, Xinjiang. *Earth Sci. Front.* **2020**, *27*, 254–275. (In Chinese)
27. Gu, X.X.; Zhang, Y.M.; Ge, Z.L.; Chen, W.Z. Mineralization and genesis of the orogenic gold system in the Kalamaili area, East Junggar, Xinjiang, northwestern China. *GSA Bull.* **2023**, *6*. [\[CrossRef\]](#)
28. Li, J.Y.; Yang, T.N.; Li, Y.P.; Zhu, Z.X. Geological features of the Karamaili faulting belt, eastern Junggar region, Xinjiang, China and its constraints on the reconstruction of Late Paleozoic ocean-continent framework of the Central Asian region. *Geol. Bull. China* **2009**, *28*, 1817–1826. (In Chinese)
29. Zhang, Y.Y.; Pe-Piper, G.; Piper, D.J.W.; Guo, Z.J. Early Carboniferous collision of the Kalamaili orogenic belt, North Xinjiang, and its implications: Evidence from molasse deposits. *GSA Bull.* **2013**, *125*, 932–944. [\[CrossRef\]](#)
30. Song, P.; Wang, T.; Tong, Y.; Zhang, J.J.; Huang, H. Late Carboniferous intrusions along the Kalamaili suture zone, southwestern Central Asian Orogenic Belt (CAOB): Implications for a tectonic switch from subduction to collision. *Int. Geol. Rev.* **2023**, *65*, 1601–1621. [\[CrossRef\]](#)
31. Xu, B.; Lu, Y.M.; Gu, X.X.; Zhang, W.Z. Characteristics of ore-forming fluids and O, H, S isotopic geochemistry of the gold deposits in the Kalamaili Area, Xinjiang, China. *Earth Sci. Front.* **2010**, *17*, 227–240. (In Chinese)
32. Nie, X.Y. Carboniferous Granitic Magma Activity and Gold Mineralization in the Kalamaili Region, Northern Xinjiang. Ph.D. Thesis, China University of Geosciences, Beijing, China, 2017. (In Chinese).
33. Xiao, W.J.; Windley, B.F.; Yuan, C.; Sun, M.; Han, C.M.; Lin, S.F.; Chen, H.L.; Yan, Q.R.; Liu, D.Y.; Qin, K.Z.; et al. Paleozoic multiple subduction-accretion processes of the southern Altaids. *Am. J. Sci.* **2009**, *309*, 221–270. [\[CrossRef\]](#)
34. Jahn, B.M.; Wu, F.Y.; Chen, B. Granitoids of the Central Asian Orogenic Belt and continental growth in the Phanerozoic. *Earth Environ. Sci. Trans. R. Soc. Edinb.* **2000**, *91*, 181–193.
35. Chen, B.; Jahn, B.M. Genesis of post-collisional granitoids and basement nature of the Junggar Terrane, NW China: Nd-Sr isotope and trace element evidence. *J. Asian Earth Sci.* **2004**, *23*, 691–703. [\[CrossRef\]](#)
36. Guo, L.S.; Zhang, R.; Liu, Y.L.; Xu, F.J.; Su, L. Zircon U-Pb age of Tonghualing intermediate-acid intrusive rocks, Eastern Junggar, Xinjiang. *Acta Sci. Nat. Univ. Pekin.* **2009**, *1*, 22–27. (In Chinese)
37. Han, B.F.; Ji, J.Q.; Song, B.; Chen, L.H.; Zhang, L. Late Paleozoic vertical growth of continental crust around the Junggar Basin, Xinjiang, China (Part I): Timing of post-collisional plutonism. *Acta Petrol. Sin.* **2006**, *22*, 1077–1086. (In Chinese)
38. Yang, G.X.; Li, Y.J.; Wu, H.E.; Zhong, X.; Yang, B.K.; Yan, C.X.; Yan, J.; Si, G.H. Geochronological and geochemical constraints on petrogenesis of the Huangyangshan A-type granite from the East Junggar, Xinjiang, NW China. *J. Asian Earth Sci.* **2011**, *40*, 722–736. [\[CrossRef\]](#)
39. Liu, W.; Liu, X.J.; Liu, L.J. Underplating generated A- and I-type granitoids of the East Junggar from the lower and the upper oceanic crust with mixing of mafic magma: Insights from integrated zircon U-Pb ages, petrography, geochemistry and Nd-Sr-Hf isotopes. *Lithos* **2013**, *179*, 293–319. [\[CrossRef\]](#)
40. Han, Y.G.; Zhao, G.C. Final amalgamation of the Tianshan and Junggar orogenic collage in the southwestern Central Asian Orogenic Belt: Constraints on the closure of the Paleo-Asian Ocean. *Earth Sci. Rev.* **2018**, *186*, 129–152. [\[CrossRef\]](#)
41. Li, J.Y. Main Characteristics and emplacement process of the East Junggar ophiolites, Xinjiang, China. *Acta Petrol. Sin.* **1995**, *11*, 73–84.
42. Fang, A.M.; Wang, S.G.; Zhang, J.M.; Zang, M.; Fang, J.H.; Hu, J.M. The U-Pb ages of zircons from the gabbro in the Kalamaili ophiolite, North Xinjiang and its tectonic significances. *Chin. J. Geol.* **2015**, *50*, 140–154. (In Chinese)
43. Wang, B.Y.; Jiang, C.Y.; Li, Y.J.; Wu, H.E.; Xia, Z.D.; Lu, R.H. Geochemistry and tectonic implications of Karamaili ophiolite in East Junggar of Xinjiang. *J. Mineral. Petrol.* **2009**, *29*, 74–82. (In Chinese)
44. Huang, G.; Niu, G.Z.; Wang, X.L.; Guo, J.; Yu, F. Formation and emplacement age of Karamaili ophiolite: LA-ICP-MS zircon U-Pb age evidence from the diabase and tuff in eastern Junggar, Xinjiang. *Geol. Bull. China* **2012**, *31*, 1267–1278. (In Chinese)
45. Tang, H.F.; Su, Y.P.; Liu, C.Q.; Hou, G.S.; Wang, Y.B. Zircon U-Pb age of the plagiogranite in Kalamaili belt, northern Xinjiang and its tectonic implications. *Geotecton. Metallog.* **2007**, *31*, 110–117. (In Chinese)

46. Qin, B. Time constraints and SHRIMP of zircon from plagioclase granite of ophiolitic in Aletunkunduo. *Northwest. Geol.* **2012**, *45*, 20–25. (In Chinese)
47. Zhao, L.; Ji, J.Q.; Xu, Q.Q.; Gong, J.F.; Tu, J.Y.; Wang, J.D. Karamaili strike-slipping fault and deformational sequence since Late Paleozoic in the northern Xinjiang. *Acta Petrol. Sin.* **2010**, *28*, 2257–2268. (In Chinese)
48. Garofalo, P.; Matthäi, S.K.; Heinrich, C.A. Three-dimensional geometry, ore distribution and time-integrated mass transfer through the quartz-tourmaline-gold vein network of the Sigma deposit (Abitibi belt, Canada). *Geofluids* **2002**, *2*, 217–232. [\[CrossRef\]](#)
49. Sibson, R.H.; Robert, F.; Poulsen, K.H. High-angle reverse faults, fluid-pressure cycling, and mesothermal gold-quartz deposits. *Geology* **1988**, *16*, 551–555. [\[CrossRef\]](#)
50. Cox, S.F.; Sun, S.S.; Etheridge, M.A.; Wall, V.J.; Potter, T.F. Structural and geochemical controls on the development of turbidite-hosted gold quartz vein deposits, Wattle Gully mine, central Victoria, Australia. *Econ. Geol.* **1995**, *90*, 1722–1746. [\[CrossRef\]](#)
51. Bodnar, R.J. Revised equation and table for determining the freezing point depression of H₂O–NaCl solutions. *Geochim. Cosmochim. Acta* **1993**, *57*, 683–684. [\[CrossRef\]](#)
52. Brown, P.E.; Lamb, W.M. P–V–T properties of fluids in the system H₂O±CO₂±NaCl: New graphical presentations and implications for fluid inclusion studies. *Geochim. Cosmochim. Acta* **1989**, *53*, 1209–1221. [\[CrossRef\]](#)
53. Brown, P.E. FLINCOR: A microcomputer program for the reduction and investigation of fluid-inclusion data. *Am. Mineral.* **1989**, *74*, 1390–1393.
54. Clayton, R.N.; Mayeda, T.K. The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. *Geochim. Cosmochim. Acta* **1963**, *27*, 43–52. [\[CrossRef\]](#)
55. Clayton, R.N.; O’Neil, J.R.; Mayeda, T.K. Oxygen isotope exchange between quartz and water. *J. Geophys. Res.* **1972**, *77*, 3057–3067. [\[CrossRef\]](#)
56. Sláma, J.; Košler, J.; Condon, D.J.; Crowley, J.L.; Gerdes, A.; Hanchar, J.M.; Horstwood, M.S.A.; Morris, G.A.; Nasdala, L.; Norberg, N.; et al. Plešovice zircon—A new natural reference material for U–Pb and Hf isotopic microanalysis. *Chem. Geol.* **2008**, *249*, 1–35. [\[CrossRef\]](#)
57. Liu, Y.S.; Hu, Z.C.; Gao, S.; Günther, D.; Xu, J.; Gao, C.G.; Chen, H.H. In situ analysis of major and trace elements of anhydrous minerals by LA-ICP-MS without applying an internal standard. *Chem. Geol.* **2008**, *257*, 34–43. [\[CrossRef\]](#)
58. Ludwig, K.R. *User’s Manual for Isoplot/ex Version 3.00: A Geochronological Toolkit for Microsoft Excel*; Special Publication; Berkeley Geochronology Center: Berkeley, CA, USA, 2003.
59. Boyle, R.W. The geochemistry of gold and its deposits. *Geol. Surv. Can. Bull.* **1979**, *280*, 1–584.
60. Youngson, J.H.; Wopereis, P.; Kerr, L.C.; Craw, D. Au–Ag–Hg and Au–Ag alloys in Nokomai and Nevis valley placers, northern Southland and Central Otago, New Zealand, and their implications. *N. Z. J. Geol. Geop.* **2002**, *45*, 53–69. [\[CrossRef\]](#)
61. Simon, G.; Kesler, S.E.; Chrysosoulis, S. Geochemistry and textures of gold-bearing arsenian pyrite, Twin Creeks, Nevada: Implications for deposition of gold in Carlin-type deposits. *Econ. Geol.* **1999**, *94*, 405–422. [\[CrossRef\]](#)
62. Goldfarb, R.J.; Baker, T.; Dubé, B.; Groves, D.I.; Hart, C.J.R.; Gosselin, P. Distribution, character, and genesis of gold deposits in metamorphic terranes. *Econ. Geol.* **2005**, *100*, 407–450.
63. Zhou, Z.J.; Chen, Y.J.; Jiang, S.Y.; Zhao, H.X.; Qin, Y.; Hu, C.J. Geology, geochemistry and ore genesis of the Wenyu gold deposit, Xiaolinling gold field, Qinling Orogen, southern margin of North China Craton. *Ore Geol. Rev.* **2014**, *59*, 1–20. [\[CrossRef\]](#)
64. Gao, H.Z.; Zhang, W.S. Characteristics and metallogenic fluid and thermodynamic condition analysis of metallogenic system in highly strained structural belt, East Junggar. *Earth Sci.-J. China Univ. Geosci.* **2000**, *25*, 369–374. (In Chinese)
65. Hoskin, P.W.O. Patterns of chaos: Fractal statistics and the oscillatory chemistry of zircon. *Geochim. Cosmochim. Acta* **2000**, *64*, 1905–1923. [\[CrossRef\]](#)
66. Hoskin, P.W.O.; Schaltegger, U. The composition of zircon and igneous and metamorphic petrogenesis. *Rev. Mineral. Geochem.* **2003**, *53*, 27–62. [\[CrossRef\]](#)
67. Wang, J.; Su, Y.P.; Zheng, J.P.; Belousova, E.A.; Griffin, W.L.; Zhou, X.; Dai, H.K. Hidden Eoarchean crust in the southwestern Central Asian Orogenic Belt. *Lithos* **2020**, *360–361*, 105437. [\[CrossRef\]](#)
68. Hoskin, P.W.O. Trace-element composition of hydrothermal zircon and the alteration of Hadean zircon from the Jack Hills, Australia. *Geochim. Cosmochim. Acta* **2005**, *69*, 637–648. [\[CrossRef\]](#)
69. Kirkland, C.L.; Whitehouse, M.J.; Slagstad, T. Fluid-assisted zircon and monazite growth within a shear zone: A case study from Finnmark, Arctic Norway. *Contrib. Mineral. Petrol.* **2009**, *158*, 637–657. [\[CrossRef\]](#)
70. McDonough, W.F.; Sun, S.S. The composition of the Earth. *Chem. Geol.* **1995**, *120*, 223–253. [\[CrossRef\]](#)
71. Cabri, L.J.; Newville, M.; Gordon, R.A.; Crozier, E.D.; Sutton, S.R.; McMahon, G.; Jiang, D.T. Chemical speciation of gold in arsenopyrite. *Can. Mineral.* **2000**, *38*, 1265–1281. [\[CrossRef\]](#)
72. Chen, Y.L.; Li, H.; Zheng, C.Y.; Elatikpo, S.M.; Cheng, S.L.; Jiang, W.T. Ore-forming process of the Haigou gold deposit in the eastern Central Asian Orogenic Belt, NE China: Constrains from EPMA and LA-ICP-MS analysis of Au-bearing pyrite. *Resour. Geol.* **2022**, *72*, e12304. [\[CrossRef\]](#)
73. Liu, H.M.; Beaudoin, G. Geochemical signatures in native gold derived from Au-bearing ore deposits. *Ore Geol. Rev.* **2021**, *132*, 104066. [\[CrossRef\]](#)
74. Harris, D.C. The mineralogy of gold and its relevance to gold recoveries. *Miner. Depos.* **1990**, *25*, S3–S7. [\[CrossRef\]](#)
75. Deditius, A.P.; Reich, M.; Kesler, S.E.; Utsunomiya, S.; Chrysosoulis, S.L.; Walshe, J.; Ewing, R.C. The coupled geochemistry of Au and As in pyrite from hydrothermal ore deposits. *Geochim. Cosmochim. Acta* **2014**, *140*, 644–670. [\[CrossRef\]](#)

76. Li, H.; Zhu, D.P.; Algeo, T.J.; Li, M.; Jiang, W.C.; Chen, S.F.; Elatikpo, S.M. Pyrite trace element and S-Pb isotopic evidence for contrasting sources of metals and ligands during superimposed hydrothermal events in the Dongping gold deposit, North China. *Miner. Depos.* **2023**, *58*, 337–358. [\[CrossRef\]](#)
77. Reich, M.; Kesler, S.E.; Utsunomiya, S.; Palenik, C.S.; Chrysosoulis, S.L.; Ewing, R.C. Solubility of gold in arsenian pyrite. *Geochim. Cosmochim. Acta* **2005**, *69*, 2781–2796. [\[CrossRef\]](#)
78. Cabri, L.J.; Chrysosoulis, S.L.; de Villiers, J.P.R.; Laflamme, J.G.; Buseck, P.R. The nature of “invisible” gold in arsenopyrite. *Can. Mineral.* **1989**, *27*, 353–362.
79. Fougereuse, D.; Reddy, S.M.; Aylmore, M.; Yang, L.; Guagliardo, P.; Saxey, D.W.; Rickard, W.D.A.; Timms, N. A new kind of invisible gold in pyrite hosted in deformation-related dislocations. *Geology* **2021**, *49*, 1225–1229. [\[CrossRef\]](#)
80. Böhlke, J.K.; Kistler, R.W. Rb-Sr, K-Ar, and stable isotope evidence for the ages and sources of fluid components of gold-bearing quartz veins in the northern Sierra Nevada foothills metamorphic belt, California. *Econ. Geol.* **1986**, *81*, 296–322. [\[CrossRef\]](#)
81. Jia, Y.F.; Li, X.; Kerrich, R. Stable isotope (O, H, S, C, and N) systematics of quartz vein systems in the turbidite-hosted Central and North Deborah gold deposits of the Bendigo gold field, central Victoria, Australia: Constraints on the origin of ore-forming fluids. *Econ. Geol.* **2001**, *96*, 705–721. [\[CrossRef\]](#)
82. Chen, H.Y.; Chen, Y.J.; Baker, M. Isotopic geochemistry of the Sawayaerdun orogenic-type gold deposit, Tianshan, northwest China: Implications for ore genesis and mineral exploration. *Chem. Geol.* **2012**, *310–311*, 1–11. [\[CrossRef\]](#)
83. Ridley, J.R.; Diamond, L.W. Fluid chemistry of orogenic lode gold deposits and implications for genetic models. *Rev. Econ. Geol.* **2000**, *13*, 146–162.
84. Goldfarb, R.J.; Newberry, R.J.; Pickthorn, W.J.; Gent, C.A. Oxygen, hydrogen, and sulfur isotope studies in the Juneau gold belt, southeastern Alaska: Constraints on the origin of hydrothermal fluids. *Econ. Geol.* **1991**, *86*, 66–80. [\[CrossRef\]](#)
85. Zhang, J.; Chen, Y.J.; Pirajno, F.; Deng, J.; Chen, H.Y.; Wang, C.M. Geology, C-H-O-S-Pb isotope systematics and geochronology of the Yindongpo gold deposit, Tongbai Mountains, central China: Implication for ore genesis. *Ore Geol. Rev.* **2013**, *53*, 343–356. [\[CrossRef\]](#)
86. Liu, J.Y.; Yu, H.X.; Wu, G.Q. Alkali granites and tin deposits of the Kalamaili area, northern Xinjiang. *Geological. Explor. Non-Ferr. Met.* **1997**, *6*, 129–135. (In Chinese)
87. Taylor, H.P. The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition. *Econ. Geol.* **1974**, *69*, 843–883. [\[CrossRef\]](#)
88. Wilkinson, J.J. Fluid inclusions in hydrothermal ore deposits. *Lithos* **2001**, *55*, 229–272. [\[CrossRef\]](#)
89. Coulbaly, Y.; Boiron, M.C.; Cathelineau, M.; Kouamelan, A.N. Fluid immiscibility and gold deposition in the Birimian quartz veins of the Angovia deposit (Yaouré, Ivory Coast). *J. Afr. Earth Sci.* **2008**, *50*, 234–254. [\[CrossRef\]](#)
90. Deng, X.H.; Chen, Y.J.; Santosh, M.; Yao, J.M. Genesis of the 1.76 Ga Zhaiwa Mo-Cu and its link with the Xiong'er volcanics in the North China Craton: Implications for accretionary growth along the margin of the Columbia supercontinent. *Precamb. Res.* **2013**, *227*, 337–348. [\[CrossRef\]](#)
91. Craw, D.; Teagle, D.A.H.; Belocky, R. Fluid immiscibility in late-Alpine gold-bearing veins, Eastern and Northwestern European Alps. *Miner. Depos.* **1993**, *28*, 28–36. [\[CrossRef\]](#)
92. Bowers, T.S.; Helgeson, H.C. Calculation of the thermodynamic and geochemical consequences of nonideal mixing in the system H₂O-CO₂-NaCl on phase relations in geologic systems: Metamorphic equilibria at high pressures and temperatures. *Am. Mineral.* **1983**, *68*, 1059–1075.
93. Ramboz, C.; Pichavant, M.; Weisbrod, A. Fluid immiscibility in natural processes: Use and misuse of fluid inclusion data: II. Interpretation of fluid inclusion data in terms of Immiscibility. *Chem. Geol.* **1982**, *37*, 29–46. [\[CrossRef\]](#)
94. Robert, F.; Kelly, W.C. Ore-forming fluids in Archean gold-bearing quartz veins at the Sigma Mine, Abitibi greenstone belt, Quebec, Canada. *Econ. Geol.* **1987**, *82*, 1464–1482. [\[CrossRef\]](#)
95. Xu, Y.F.; Ni, P.; Wang, G.G.; Pan, J.Y.; Guan, S.J.; Chen, H.; Ding, J.Y.; Li, L. Geology, fluid inclusion and stable isotope study of the Huangshan orogenic gold deposit: Implications for future exploration along the Jiangshan-Shaoxing fault zone, South China. *J. Geochem. Explor.* **2016**, *171*, 37–54. [\[CrossRef\]](#)
96. Roedder, E. Fluid inclusions: Reviews in Mineralogy and Geochemistry. *Mineral. Soc. Am.* **1984**, *12*, 1–644.
97. Hollister, L.S. Enrichment of CO₂ in fluid inclusions in quartz by removal of H₂O during crystal-plastic deformation. *J. Struct. Geol.* **1990**, *12*, 895–901. [\[CrossRef\]](#)
98. Hall, D.L.; Bodnar, R.J. Methane in fluid inclusions from granulites: A product of hydrogen diffusion? *Geochim. Cosmochim. Acta* **1990**, *54*, 641–651. [\[CrossRef\]](#)
99. Benning, L.G.; Seward, T.M. Hydrosulphide complexing of Au(I) in hydrothermal solutions from 150–400 °C and 500–1500 bar. *Geochim. Cosmochim. Acta* **1996**, *60*, 1849–1871. [\[CrossRef\]](#)
100. Stefánsson, A.; Seward, T.M. Gold(I) complexing in aqueous sulphide solutions to 500 °C at 500 bar. *Geochim. Cosmochim. Acta* **2004**, *68*, 4121–4143. [\[CrossRef\]](#)
101. Phillips, G.N.; Powell, R. Formation of gold deposits: A metamorphic devolatilization model. *J. Metamorph. Geol.* **2010**, *28*, 689–718. [\[CrossRef\]](#)
102. Phillips, G.N.; Evans, K.A. Role of CO₂ in the formation of gold deposits. *Nature* **2004**, *429*, 860–863. [\[CrossRef\]](#)
103. Neall, F.B.; Phillips, G.N. Fluid-wall rock interaction in an Archean hydrothermal gold deposit: A thermodynamic model for the Hunt Mine, Kambalda. *Econ. Geol.* **1987**, *82*, 1679–1694. [\[CrossRef\]](#)

104. Naden, J.; Shepherd, T.J. Role of methane and carbon dioxide in gold deposition. *Nature* **1989**, *342*, 793–795. [\[CrossRef\]](#)
105. Lee, J.K.W.; Williams, I.S.; Ellis, D.J. Pb, U and Th diffusion in natural zircon. *Nature* **1997**, *390*, 159–162. [\[CrossRef\]](#)
106. Yeats, C.J.; McNaughton, N.J.; Groves, D.I. SHRIMP U-Pb geochronological constraints on Archean volcanic-hosted massive sulfide and lode gold mineralization at Mount Gibson, Yilgarn Craton, Western Australia. *Econ. Geol.* **1996**, *91*, 1354–1371. [\[CrossRef\]](#)
107. Claoué-Long, J.C.; King, R.W.; Kerrich, R. Archean hydrothermal zircon in the Abitibi greenstone belt: Constraints on the timing of gold mineralisation. *Earth Planet. Sci. Lett.* **1990**, *98*, 109–128. [\[CrossRef\]](#)
108. Kerrich, R.; King, R. Hydrothermal zircon and baddeleyite in Val-d’Or Archean mesothermal gold deposits: Characteristics, compositions, and fluid-inclusion properties, with implications for timing of primary gold mineralization. *Can. J. Earth Sci.* **1993**, *30*, 2334–2351. [\[CrossRef\]](#)
109. Xu, J.C.; Gu, X.X.; Zhang, Y.M.; Wang, J.L.; He, G.; Zhou, C.; Liu, R.P. Geology, fluid inclusions, HO isotope, and hydrothermal zircon U-Pb geochronology of the Daqingshan orogenic gold deposit in Beishan orogenic belt, Xinjiang, NW China. *Miner. Depos.* **2021**, *56*, 325–342. [\[CrossRef\]](#)
110. Deng, X.D.; Li, J.W.; Wen, G. U-Pb geochronology of hydrothermal zircons from the early Cretaceous iron skarn deposits in the Handan-Xingtai district, North China craton. *Econ. Geol.* **2015**, *110*, 2159–2180. [\[CrossRef\]](#)
111. Li, X.; Wang, K.Y.; Sun, G.S.; Sun, J.D.; Liu, G.Y.; Zhang, J.T.; Han, L.; Wang, G.W. Discussion on metallogenesis of Zhaojiagou Ta-Nb deposit in Inner Mongolia: Evidence from amazonitization and albitization granite geochronology and geochemistry. *Acta Petrol. Sin.* **2021**, *37*, 1765–1784. (In Chinese)
112. Li, X.C.; Fan, H.R.; Zeng, X.; Yang, K.F.; Yang, Z.F.; Wang, Q.W.; Li, H.T. Identification of ~1.3 Ga hydrothermal zircon from the giant Bayan Obo REE deposit (China): Implication for dating geologically-complicated REE ore system. *Ore Geol. Rev.* **2021**, *138*, 104405. [\[CrossRef\]](#)
113. Zhang, S.; Zhou, T.F.; Zhang, Z.Z.; Wu, M.A.; Wang, J.; Lü, Q.T. In-situ hydrothermal zircon U-Pb and phlogopite ⁴⁰Ar-³⁹Ar geochronology of uranium mineralisation in Luzong ore district scientific drilling (LTZK01), Anhui Province, SE China: Constraints on the mineralisation process. *Ore Geol. Rev.* **2021**, *134*, 104133. [\[CrossRef\]](#)
114. Jiang, W.C.; Li, H.; Evans, N.J.; Wu, J.H. Zircon records multiple magmatic-hydrothermal processes at the giant Shizhuyuan W-Sn-Mo-Bi polymetallic deposit, South China. *Ore Geol. Rev.* **2019**, *115*, 103160. [\[CrossRef\]](#)
115. Elatikpo, S.M.; Li, H.; Liu, B.; Zhang, W.D. Metallogenesis of the Bakoshi-Kundila gold deposit in northern West Nigerian Subshield: Insights from pyrite chemical and sulfur isotopic compositions and zircon U-Pb geochronology. *Precamb. Res.* **2022**, *383*, 106890. [\[CrossRef\]](#)
116. Dubińska, E.; Bylina, P.; Kozłowski, A.; Dörr, W.; Nejbert, K.; Schastok, J.; Kulicki, C. U-Pb dating of serpentinization: Hydrothermal zircon from a metasomatic rodingite shell (Sudetic ophiolite, SW Poland). *Chem. Geol.* **2004**, *203*, 183–203. [\[CrossRef\]](#)
117. Dempster, T.J.; Hay, D.C.; Bluck, B.J. Zircon growth in slate. *Geology* **2004**, *32*, 221–224. [\[CrossRef\]](#)
118. Zhai, W.; Zhang, E.; Zheng, S.Q.; Santosh, M.; Sun, X.M.; Niu, H.C.; Fu, B.; Fu, Y.; Li, D.F.; Jiang, Y.H.; et al. Hydrothermal zircon: Characteristics, genesis and metallogenic implications. *Ore Geol. Rev.* **2022**, *149*, 105111. [\[CrossRef\]](#)
119. Fan, T.T.; Zhou, X.H.; Liu, Y.Q.; Li, W.; Zheng, Z.Y.; Hu, T.; Liang, H. Crystal tuff zircon LA-ICP-MS U-Pb ages from the Lower Jiangbasitao Formation in the East Daheishan area, Xinjiang and their geological implications. *Acta Sedimentol. Sin.* **2011**, *29*, 312–320. (In Chinese)
120. Wang, J.; Su, Y.P.; Zheng, J.P.; Belousova, E.A.; Chen, M.; Dai, H.K.; Zhou, L. Rapid transition from oceanic subduction to postcollisional extension revealed by Carboniferous magmatism in East Junggar (NW China), southwestern Central Asian orogenic belt. *GSA Bull.* **2022**, *134*, 1018–1042. [\[CrossRef\]](#)
121. Xi, X.W.; Yang, L.Q.; Wang, Y.J.; Deng, J.; Lin, G.; Wang, J.P.; Lei, X.Q. Numerical modeling of the temperature effects of tectonic regimes transformation and their ore-forming dynamics. *Earth Sci. Front.* **2003**, *10*, 47–55. (In Chinese)
122. Li, H.Q.; Chen, F.W. *Regional Mineralization in Altay Area of Northern Xinjiang China*; Geological Publishing House: Beijing, China, 2004; pp. 1–391. (In Chinese)
123. Lu, Y.M.; Zhang, Y.J.; Pan, M.; Fan, J.J.; Liu, Y.F.; Zhang, D.; Chen, X.W.; Pan, A.J. Types and geological characteristics of gold deposits in East Junggar, Xinjiang. *Acta Geosci. Sin.* **2010**, *31*, 434–442. (In Chinese)
124. Chen, W.Z.; Gu, X.X.; Zhang, Y.M.; He, G.; Huang, G.; Li, J.T. Geological features and geochronology of the Jinshuiquan gold deposit in the East Junggar, Xinjiang. *Geol. Bull. China* **2019**, *38*, 1240–1255. (In Chinese)
125. Liu, J.; Bao, X.S.; Gao, Y.B.; Yang, K.; Kou, S.L.; Yang, W.; Wang, Z.B.; He, J.L.; Zhang, Y.X.; Chen, H. Composition and Geochemical Characteristics of Pyrite and Quartz: Constraints on the Origin of the Xinjiazui Gold Deposit, Northwestern Margin of the Yangtze Block, China. *Minerals* **2022**, *12*, 688. [\[CrossRef\]](#)

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