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Ore Genesis of the Lower Urgen Porphyry Molybdenum Deposit in the Northern Great Xing'an Range, Northeast China: Constraints from Molybdenite Re-Os Dating, Fluid Inclusions, and H-O-S-Pb Isotopes

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Abstract: The Lower Urgen molybdenum deposit (44,856 t Mo @ 0.141%), situated in the northern Great Xing'an Range, is a newly discovered porphyry molybdenum deposit. Mineralization is characterized by veinlet-disseminated- and vein-type quartz–sulfide orebodies primarily occurring in the cupola of the Early Cretaceous granite porphyry stock. In this study, we present a detailed description of the ore geology, molybdenite Re-Os dating, H-O-S-Pb isotopic compositions, and fluid inclusion (FI) analyses including petrography, laser Raman, and microthermometry to precisely constrain the timing of ore formation, the origin of ore-forming fluids and materials, as well as the metal precipitation mechanism. Molybdenite Re-Os dating yielded two model ages of 141.2 ± 1.5 and 147.7 ± 1.7 Ma, coeval with the regional Late Jurassic–Early Cretaceous molybdenum metallogenesis. The hydrothermal process can be divided into three stages: the quartz–molybdenite(–pyrite) stage, quartz–polymetallic sulfide stage, and quartz–carbonate stage. Four types of FIs were distinguished for quartz, including two-phase liquid-rich (L-type), saline (S-type), CO₂-rich (C1-type), and CO₂-bearing (C2-type) FIs. Microthermometric data showed that the homogenization temperatures and salinities from the early to late stages were 240–430 °C, 5.0–11.9, and 30.1–50.8 wt% NaCl equiv.; 180–280 °C and 3.0–9.1 wt% NaCl equiv.; and 120–220 °C and 0.2–7.9 wt% NaCl equiv., respectively, suggesting a decreasing trend. H-O isotopic compositions indicate that the ore-forming fluids were initially of magmatic origin with the increasing incorporation of meteoric water. S-Pb isotopic compositions indicate that the ore-forming materials originated from granitic magmas, and the mineralization is genetically related to the ore-bearing granite porphyry stock in the deposit. Fluid immiscibility and fluid–rock interaction are collectively responsible for the massive deposition of molybdenite in stage 1, whereas fluid mixing and immiscibility played a critical role in the deposition of polymetallic sulfide in stage 2.

Keywords: molybdenite Re-Os dating; fluid inclusions; H-O-S-Pb isotopes; lower urgen molybdenum deposit; NE China

1. Introduction

Porphyry deposits are commonly spatially, temporally, and genetically related to intermediate–acid hypabyssal porphyry intrusions [1], and provide more than 75%, 50%, and 20% of the world’s molybdenum, copper, and gold resources, respectively [2–5]. Mineralization mainly occurs as veinlets and disseminations concentrated in or near the cupolas of porphyry intrusions, and is related to the hydraulic fracturing resulting from fluid exsolution from magmas [3,6,7]. Taking the economic importance of porphyry molybdenum deposits into account, the study of the genesis and metallogenic models of these deposits has always been an essential subject in ore deposit research [8–16].

China has the largest molybdenum resources worldwide, accounting for about 54% of the world’s known economic molybdenum resources [17], which appear in six predominant molybdenum metallogenic provinces, i.e., NE China, Qinling–Dabie, Yanliao, Sanjiang, the middle-lower Yangtze River Valley, and South China [18]. NE China is situated in the eastern Central Asian Orogenic Belt (CAOB) tectonically. A long-term tectonomagmatic evolutionary history has made it a significant polymetallic metallogenic province around the world [19–25] (Figure 1). More than 11.4 Mt of molybdenum has now been discovered in NE China, including 4 super-large (>0.5 Mt Mo), 11 large (0.1–0.5 Mt Mo), 22 medium (0.01–0.1 Mt Mo), and 18 small (<0.01 Mt Mo) molybdenum deposits, marking NE China as the largest molybdenum metallogenic province in China [26] (Figure 1c).

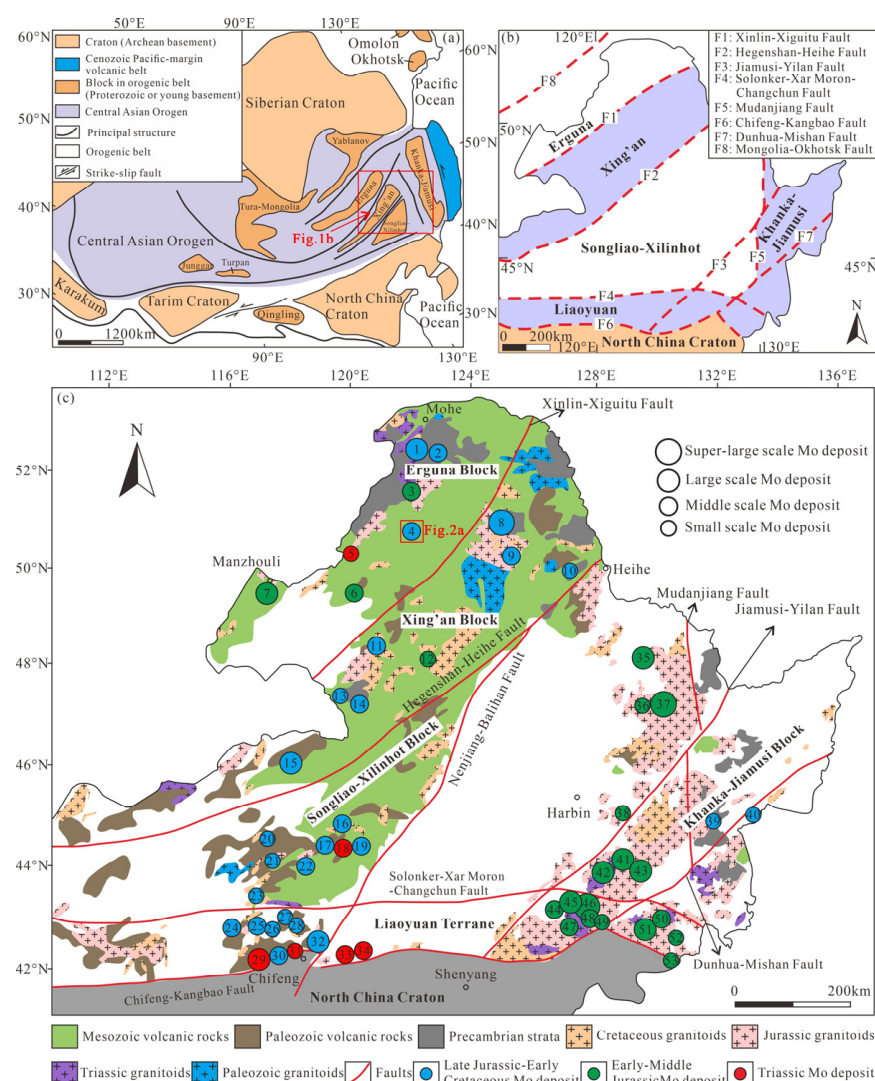


Figure 1. (a) Simplified tectonic map of the Central Asian Orogenic Belt (modified from [27,28]). (b) Schematic tectonic map of NE China (modified from [29]). (c) Distribution of major molybdenum

deposits in NE China (modified from [20]). Deposit locations: 1—Jiliuhe; 2—Fukeshan; 3—Taipingchuan; 4—Lower Urgen; 5—Badaguan; 6—Zishi; 7—Wunugetushan; 8—Chalukou; 9—Daheishan; 10—Yezhugou; 11—Taipinggou; 12—Baojiagou; 13—Nanxingan; 14—Jiazishan; 15—Diyanqinamu; 16—Aolunhua; 17—Banlashan; 18—Laojiagou; 19—Haolibao; 20—Hashitu; 21—Erbadi; 22—Yangchang; 23—Longtoushan; 24—Hongshanzi; 25—Xiaodonggou; 26—Liutiaogou; 27—Gangzi; 28—Tuohe; 29—Chehugou; 30—Nianzigou; 31—Yuanbaoshan; 32—Jiguanshan; 33—Baimashi; 34—Kulitu; 35—Huojihe; 36—Cuiling; 37—Luming; 38—Wudaoling; 39—Kanchuangou; 40—Jinchanggou; 41—Fuanpu; 42—Jidetun; 43—Dashihe; 44—Houdaomu; 45—Xingshan; 46—Daheishan; 47—Sangedingzi; 48—Sifangdianzi; 49—Xinhualong; 50—Liushengdian; 51—Sanchazi; 52—Dongfeng; 53—Shirengou.

The Lower Urgen deposit in Inner Mongolia, NE China, is a newly discovered porphyry molybdenum deposit, with estimated reserves of 44,856 t of molybdenum at an average grade of 0.141% [30]. The geochronology, petrogenesis, and tectonic context of the barren granites in the mining area have been the primary subjects of earlier investigations of the deposit [31]. Nonetheless, the direct timing of molybdenum mineralization, ore-forming fluids and the metal source, and metallogenic processes remains enigmatic. In accordance with a thorough field investigation and petrographic observations of thin sections, we present comprehensive descriptions of the geology, mineralization stages, and hydrothermal alteration in the Lower Urgen molybdenum deposit. The new molybdenite Re-Os geochronology, fluid inclusion (FI) study (petrography, laser Raman, and microthermometry analyses), and isotope geochemistry (H-O-S-Pb) for the deposit are investigated. By combining our results with available geochronology and geodynamic research in the region, we aim to (1) restrict the timing of molybdenum mineralization in the Lower Urgen molybdenum deposit; (2) determine ore-forming fluids and the metal source; and (3) decipher fluid evolution processes and ore precipitation mechanisms. This study not only contributes to the establishment of a plausible metallogenetic model for the Lower Urgen molybdenum deposit, but also has important implications for the comprehension of regional molybdenum metallogenesis and the future molybdenum prospecting and exploration.

2. Regional Geology

The tectonic components of NE China include the Erguna Block in the northwest, the Xing'an and Songliao-Xilinhote blocks in the central part, the Khanka-Jiamusi Block in the southeast, and the Liaoyuan Terrane in the south [28] (Figure 1). Major faults separating these tectonic units include the Hegenshan-Heihe, Solonker-Xar Moron-Changchun, Xinlin-Xiguitu, and Mudanjiang faults [28,29] (Figure 1b). NE China has experienced a multi-stage Phanerozoic tectonic evolutionary history, including the subduction and final closure of the Palaeo-Asian Ocean (PAO) during the Paleozoic to Early Mesozoic [28,32–35], the south-directed subduction and closure of the Mongol-Okhotsk Ocean (MOO), and the west-directed subduction and subsequent rollback of the Palaeo-Pacific Ocean (PPO) plate during the Mesozoic [29,36,37]. Due to the overprinting of multiple tectonic domains, NE China experienced extensive tectonomagmatic events, accompanied by intense metallogenesis [19–25]. Three episodes of Mesozoic molybdenum mineralization are recognized in the region, including the Triassic, Early–Middle Jurassic, and Late Jurassic–Early Cretaceous [18,24]. The major location of the Triassic molybdenum deposits is along the Solonker-Xar Moron-Changchun Fault (SXCF), with minor occurrences in the northern and central Great Xing'an Range (NCGXR). The Triassic molybdenum deposits near the SXCF were formed in a syn-collision compressional to post-collision extensional environment induced through the tectonic evolution of the PAO [18,38–43], whereas the Triassic molybdenum deposits in the NCGXR were formed in a subduction-dominated compressional environment induced through the SE-directed subduction of the MOO plate [44–48]. The Early–Middle Jurassic molybdenum deposits are concentrated in the Lesser Xing'an-

Zhangguangcai Range (LXZR) and sparsely distributed in the NCGXR, which were formed in a compressional environment controlled by the overprinting influence of the SE-directed subduction of the MOO plate in the west and the NW-directed subduction of the PPO plate in the east [49–64]. Molybdenum deposits from the Late Jurassic to Early Cretaceous are mostly concentrated in the GXR, with sporadic occurrences in the LXZR, which were formed in a post-orogenic extensional environment triggered by the PPO and MOO tectonic domains [56,63,65–88].

The NCGXR comprises two main units, i.e., the Erguna and Xing'an blocks (Figure 1c). The amalgamation of the Erguna and Xing'an blocks occurred along the Xinlin-Xiguitu Fault in the Early Palaeozoic induced by the closure of the PAO [28,89–92]. Volcanic-sedimentary rocks of the Xinghuadukou, Ergunahe, Jiageda, and Luomahu groups; Neoproterozoic magmatic rocks; and minor Palaeoproterozoic gneisses compose the basement of the Erguna Block [29,93,94]. Multiple Late Palaeozoic–Late Mesozoic episodes of accretion and collision occurred on the Erguna Block, resulting in the formation of tremendous intrusions, volcanics, and volcanoclastic rocks [95,96]. Widespread Mesozoic igneous rocks; Early Palaeozoic basement rocks composed of the Wolegen, Xinkailing, Zalantun, and Fengshuigouhe groups; together with the Xinghuadukou Complex and dispersed Palaeozoic plutons and sediments constitute the Xing'an Block, the primary component of the GXR [29]. Neoproterozoic granite is locally distributed in the western region [97]. Mesozoic volcanics are categorized by the Tamulangou, Manketouebo, Manitu, Baiyingaolao, and Meiletu Formations (Fms), from oldest to youngest [93]. The Palaeozoic strata were extensively emplaced through substantial Palaeozoic to Mesozoic granitic intrusions. The latest geochronological evidence indicates that the magmatism within the NCGXR took place in two periods: the Palaeozoic granites consisting of granite, monzogranite, granodiorite, quartz diorite, and syenogranite mainly distributed in the northeastern part with zircon U-Pb ages of 517–420 and 359–250 Ma; and the Mesozoic granites, comprising monzogranite, syenogranite, granodiorite, granite porphyry, quartz porphyry, and quartz monzogranite, which are more widespread than the Palaeozoic intrusions and yielded a zircon U-Pb age of 250–118 Ma [29,98–104] (Figure 1c).

3. Ore Deposit Geology

The Lower Urgen molybdenum deposit (120°27'30" E, 50°22'42" N), situated in the central NCGXR, discovered in 2017, is still in exploration and not in production (Figure 1c). The strata exposed in the mining area comprise the Tamulangou Fm of the Middle Jurassic, Manketouebo Fm of the Upper Jurassic, Baiyingaolao Fm of the Lower Cretaceous, and Quaternary [30] (Figure 2). The Tamulangou Fm comprises intermediate–basic volcanics including trachyandesite, andesite, and basaltic-trachyandesite. The Manketouebo Fm comprises felsic volcanics including volcanic breccia, rhyolite, and volcanic agglomerate. The Baiyingaolao Fm is locally dispersed in the northwestern part, which is composed of rhyolite, rhyolitic breccia lava, and tuff [30]. Mesozoic granitoids include quartz monzonite porphyry, syenite porphyry, and granite porphyry. The Middle Jurassic quartz monzonite porphyry outcrops are scattered in the western and central regions. The Early Cretaceous syenite porphyry locally occurs in the western region, while the Early Cretaceous granite porphyry outcrops are mostly distributed in the eastern region [30] (Figure 2). Zhang et al. [31] obtained precise zircon U-Pb ages of the barren quartz monzonite porphyry and syenite porphyry of 165.0 ± 2.5 Ma and 125.5 ± 1.9 Ma, respectively. Mineralization is characterized by concealed veinlet-disseminated- and vein-type quartz–sulfide orebodies mostly hosted in the cupola of the Early Cretaceous granite porphyry (Figures 2c and 3). Ore minerals are mainly molybdenite and pyrite, as well as subordinate chalcopyrite, sphalerite, arsenopyrite, and galena (Figure 3). K-feldspar, quartz, and sericite are the predominant gangue minerals, accompanied by epidote, biotite, and calcite (Figures 3g and 4). Molybdenite occurs as medium-coarse grained (1.2–7 mm) crystals with platy and leaf-like forms in ore-bearing quartz veins and granite porphyry (Figure 3a–c). Pyrite is present as euhedral to subhedral octahedral–dodecahedral crystals, and usually coexists with

molybdenite, chalcopyrite, sphalerite, and galena in granular aggregate forms (Figure 3). Sphalerite occurs as medium-coarse grained (1.5–7 mm) anhedral crystals, and is often intergrown with galena, chalcopyrite, and pyrite (Figure 3e,f,i). Chalcopyrite appears as fine-medium grained (0.4–1.3 mm) irregular crystals. It often coexists with pyrite and occurs in small amounts with galena and sphalerite (Figure 3d,e,i). Arsenopyrite is observed as rhomboid euhedral crystals (Figure 3d). Galena is observed as fine-medium-grained (0.6–4.5 mm) irregular crystals, and is often coeval with sphalerite, pyrite, and chalcopyrite in quartz veins (Figure 3e,f,i). Superposition mineralization in the cupola of the granite porphyry is ubiquitous, and no obvious metallogenic zonation is observed.

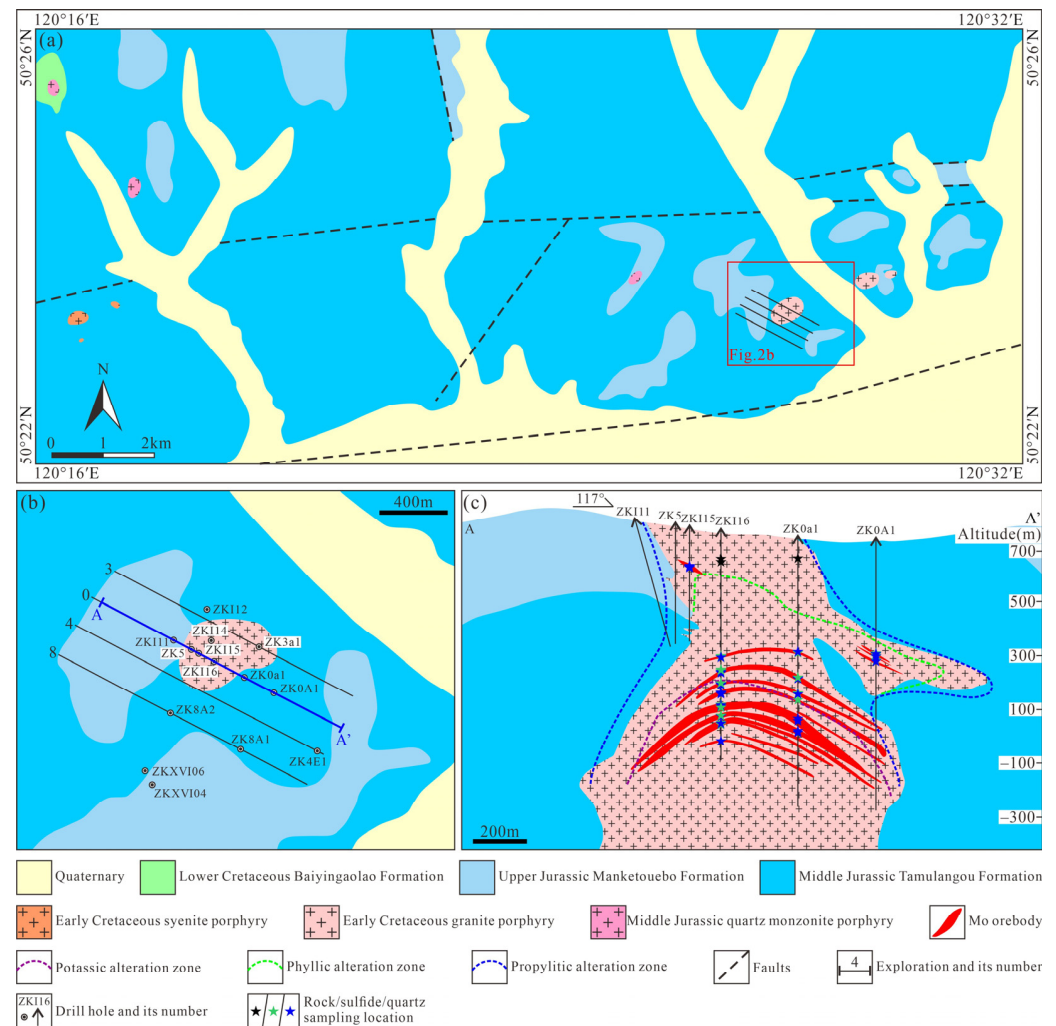


Figure 2. (a) Schematic regional geological map of the Lower Urgen molybdenum deposit. (b) Geological sketch map of the Lower Urgen molybdenum deposit. (c) Schematic geological cross-section of no. 0 exploration line (modified after [30]).

Intensive hydrothermal alteration is a defining characteristic of the Lower Urgen molybdenum deposit. There are three alteration zones recognized according to field observations and thin-section petrography: an intense potassic alteration zone at depth, a phyllic alteration zone at mid-shallow depths, and a propylitic alteration zone near the surface and periphery of the deposit. The potassic and phyllic alteration zones are all distributed in the granite porphyry, while the propylitic alteration zone mainly occurs in the intermediate–mafic volcanics around the granite porphyry. The spatial relationship of the three alteration zones is delineated in Figure 2c. The potassic alteration has a high temperature and is featured by a mineral assemblage of K-feldspar, biotite, and quartz [1,3] (Figure 4a). Quartz–molybdenite veinlets are distributed in the granite por-

phyry with intense potassic alteration (Figure 4a). The phyllic alteration is distinguished by the replacement of primary K-feldspar and plagioclase in the granite porphyry with quartz and sericite (Figure 4e). Quartz–pyrite–chalcopyrite, quartz–galena–sphalerite, and quartz–molybdenite(–pyrite) veins are usually developed in the phyllic alteration zone (Figure 4b,c). The propylitic alteration generally represents low-temperature hydrothermal alteration, which is featured by plagioclase replaced by epidote [1,3] (Figure 4d,f).

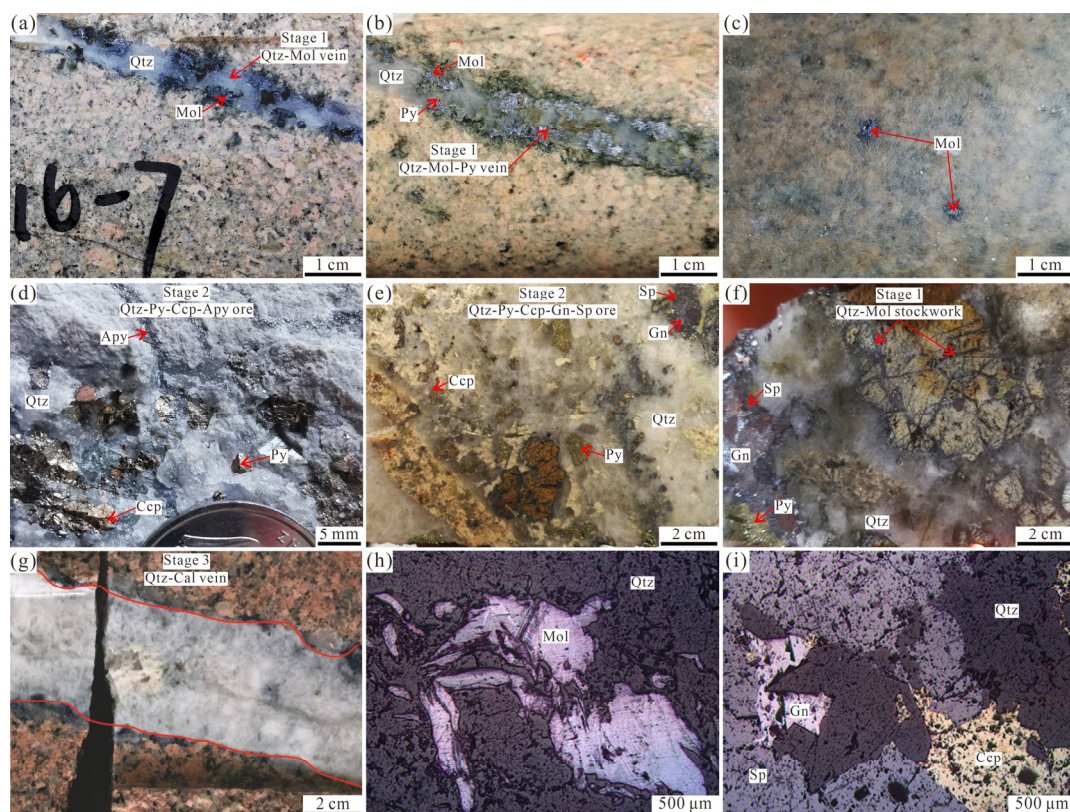


Figure 3. Representative photographs (a–g) and photomicrographs (h,i) of the mineralization in the Lower Urgen molybdenum deposit. (a) Quartz–molybdenite vein of stage 1 in the granite porphyry. (b) Quartz–molybdenite–pyrite vein of stage 1 in the granite porphyry. (c) Molybdenite occurs as disseminations. (d) Quartz–pyrite–chalcopyrite–arsenopyrite ore of stage 2. (e) Quartz–pyrite–chalcopyrite–galena–sphalerite ore of stage 2. (f) The brecciated fragments of granite porphyry containing quartz–molybdenite stockworks of stage 1 hosted by a quartz–pyrite–galena–sphalerite vein of stage 2. (g) Quartz–calcite vein of stage 3. (h) Molybdenite. (i) Galena intergrown with sphalerite. Sphalerite replacing chalcopyrite along crystal margins. Abbreviations: Mol, molybdenite; Py, pyrite; Ccp, chalcopyrite; Gn, galena; Sp, sphalerite; Apy, arsenopyrite; Qtz, quartz; Cal, calcite.

There are three main stages of hydrothermal processes in the Lower Urgen molybdenum deposit according to crosscutting relationships and mineral paragenetic sequences, including the quartz–molybdenite(–pyrite) stage (stage 1), quartz–polymetallic sulfide stage (stage 2), and quartz–carbonate stage (stage 3).

Stage 1 is the main molybdenum mineralization stage. Molybdenite, pyrite, quartz, and sericite are developed in this stage. Various types of veins were formed, including quartz–molybdenite veins and veinlets (Figures 3a and 4a), quartz–molybdenite stockworks (Figure 3f), and quartz–molybdenite–pyrite veins (Figures 3b and 4b). Disseminated molybdenite ores can also be found (Figure 3c).

Stage 2 is featured by an assemblage of chalcopyrite, sphalerite, arsenopyrite, pyrite, galena, quartz, sericite, and epidote. The most common sulfide is pyrite, which appears as fine-medium-grained euhedral to subhedral crystals and aggregates, which often form quartz–sulfide veins with chalcopyrite, galena, sphalerite, and quartz, i.e.,

quartz–pyrite–chalcopyrite–arsenopyrite veins (Figure 3d), quartz–chalcopyrite–pyrite veins (Figure 4c), quartz–pyrite–chalcopyrite–sphalerite–galena veins (Figure 3e), and quartz–pyrite–sphalerite–galena veins (Figure 3f). Galena and sphalerite are often intergrown, and they form quartz–galena–sphalerite veins and veinlets (Figure 4b,d). The brecciated fragments of granite porphyry containing stage 1 quartz–molybdenite stockworks can be found in stage 2 quartz–pyrite–sphalerite–galena veins (Figure 3f). Additionally, stage 2 quartz–galena–sphalerite veins cut stage 1 quartz–molybdenite–pyrite veins (Figure 4b).

Stage 3 represents the termination of the hydrothermal activity in the Lower Urgen molybdenum deposit. During this stage, quartz and calcite make up the majority of the veins, and sulfides are no longer found in this veins' stage (Figure 3g).

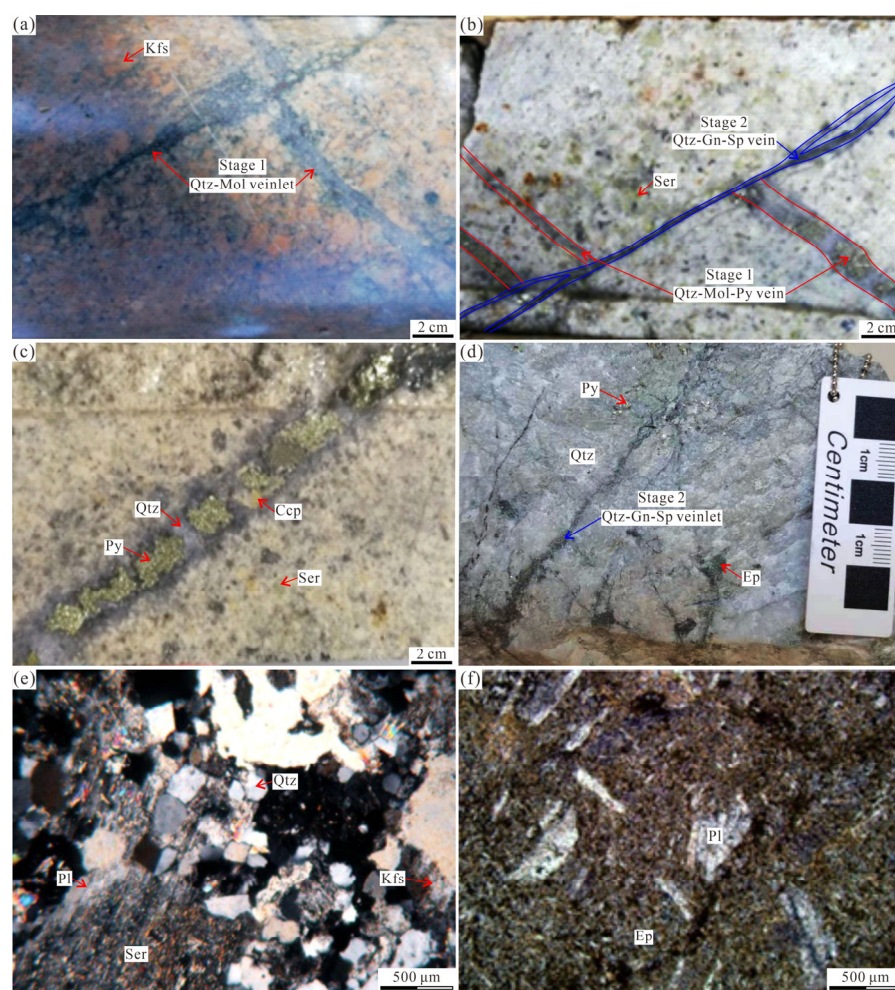


Figure 4. Representative hand specimen (a–d) and photomicrographs (crossed-polarized light) (e,f) of gangue minerals from the Lower Urgen molybdenum deposit. (a) Quartz–molybdenite veinlets of stage 1 occur in the granite porphyry with potassic alteration. (b) Quartz–molybdenite–pyrite veins of stage 1 cut by quartz–galena–sphalerite of stage 2. These ore veins occur in the granite porphyry with phyllic alteration. (c) Quartz–pyrite–chalcopyrite vein of stage 2 occurs in the granite porphyry with phyllic alteration. (d) Quartz–galena–sphalerite veinlets of stage 2 are spatially related to silicification and propylitic alteration. (e) Phyllic-altered granite porphyry is characterized by quartz and sericite replacing plagioclase along fractures and crystal margins. (f) Propylitic-altered andesite is featured with epidote replacing plagioclase. Abbreviations: Qtz, quartz; Kfs, K-feldspar; Pl, plagioclase; Ser, sericite; Ep, epidote; Mol, molybdenite; Py, pyrite; Gn, galena; Sp, sphalerite; Ccp, chalcopyrite.

4. Sampling and Analytical Methods

4.1. Samples

Samples for this study were all collected from drillholes, containing three granite porphyry samples, twenty-nine sulfide samples, and twenty-eight quartz samples. The sample locations are indicated in Figure 2c. All granite porphyry samples (T0a1-1, T0a1-2, and T16-1) were fresh and used for whole-rock Pb isotope analyses. Twenty-nine sulfide samples comprised sixteen molybdenite samples, seven pyrite samples, four chalcopyrite samples, and two galena samples. Sixteen molybdenite samples were obtained from stage 1 molybdenite(–pyrite)-bearing quartz veins, while the other sulfide samples were all collected from stage 2 sulfide-bearing quartz veins. Two molybdenite samples (G5 and LE-1) were used for Re–Os isotope analyses. Six molybdenite samples (LU16-1, LU16-2, LU16-3, LU16-4, LU16-5, and LU16-6), two pyrite samples (LU16-7 and LU16-8), two chalcopyrite samples (LU16-9 and LU16-10), and one galena sample (LU16-11) were used for S isotope analyses. Eight molybdenite samples (D17-2, D17-3, D17-4, D17-5, D17-7, D0A1-1, D0A1-2, and D0a1-1), five pyrite samples (G10-2, G11-2, G13, G14, and D17-1), two chalcopyrite samples (D17-2 and G8-2), and one galena sample (G8-3) were used for Pb isotope analyses. The quartz samples were obtained from veins of all stages, including seven samples from stage 1 molybdenite(–pyrite)-bearing quartz veins, nine samples from stage 2 sulfide-bearing quartz veins, and five samples from stage 3 quartz–carbonate veins. Seven quartz samples of stage 1 veins (B16-1, B16-2, B16-3, B16-4, B16-5, B16-6, B16-7), seven quartz samples of stage 2 veins (D14-1, D16-1, D16-4, D16-6, D16-7, D16-8, and D16-9), and three quartz samples of stage 3 veins (G8-1, G10-1, and G11-1) were used for H–O isotope analyses. Seven quartz samples of stage 1 veins (BG16-1, BG16-2, BG16-3, BG16-4, BG16-5, BG16-6, and BG16-7), two quartz samples of stage 2 veins (BG8-1 and BG14-1), and two quartz samples of stage 3 veins (BG8-2 and BG8-3) were used for the FI study. For investigations of FIs in quartz cores, thirty-six double-polished thin sections (200 µm thick) were prepared.

4.2. Molybdenite Re–Os Isotope Dating

Re–Os isotope analyses were carried out at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences in Guiyang, China. A TJA PQ ExCell ICP–MS was applied to measure the contents of Re, ^{187}Re , and ^{187}Os . We followed the analytical procedures reported in [105,106]. The Re–Os model ages were calculated using the formula $t = 1/\lambda [\ln(1 + ^{187}\text{Os}/^{187}\text{Re})]$, where λ is the decay constant for ^{187}Re ($1.666 \times 10^{-11} \text{ year}^{-1}$) [107].

4.3. FIs Laser Raman Spectroscopy

A Renishaw inVia laser Raman probe at the Beijing Createch Testing Technology Co., Ltd. in Beijing, China, was applied to examine the vapor and liquid components of quartz-hosted FIs at room temperature. For detection, a laser power of 20 mW and an argon ion laser with a wavelength of 514.5 nm were used. The spectrum was measured from 1000 to 4000 cm^{-1} with a counting time of 20 s for each scan. Detailed analytical procedures are consistent with those in [108].

4.4. FIs Microthermometry

FI microthermometry was conducted using a Linkam THMS 600 heating-freezing stage with a stage of -195 to 600°C mounted on a Zeiss microscope at the Beijing Createch Testing Technology Co., Ltd., Beijing, China. The accuracy of temperature observations is 0.2°C through cooling, $\pm 0.2^\circ\text{C}$ for 0 – 100°C , and $\pm 2^\circ\text{C}$ for 100 – 450°C . To properly record the phase transformation process, the heating rate was decreased to $0.1^\circ\text{C}/\text{min}$ close to the freezing point and $0.2^\circ\text{C}/\text{min}$ close to the homogenization temperature. To prevent unintentional deviations, FI results were only collected on FI assemblages (FIAs) [109]. During heating, seven different temperature types were recorded, including CO_2 –ice melting temperatures (T_{mCO_2}), first ice melting temperatures (T_{fmice}), final ice melting temperatures

($T_{m_{ice}}$), final clathrate melting temperatures ($T_{m_{clath}}$), CO_2 homogenization temperatures ($T_{h_{CO_2}}$), halite dissolution temperatures (T_{m_H}), and final homogenization temperatures (T_h). $T_{m_{clath}}$ was used to determine the salinities of the fluid system composed of NaCl, CO_2 , and H_2O [110]. $T_{m_{ice}}$ and T_{m_H} were used to obtain the salinities of the fluid system composed of NaCl and H_2O [111,112]. Using the Flincor program, the bulk molar volume of FIs, the density of the bulk fluids and carbonic liquid, and mole fractions of compositions were acquired [113–115].

4.5. Quartz H-O Isotopes

H-O isotope analyses were carried out using a MAT253 mass spectrometer at the Beijing Research Institute of Uranium Geology in Beijing, China. The accuracies of the H and O isotopic measurements are better than $\pm 2\text{‰}$ and $\pm 0.2\text{‰}$, respectively. The fractionation formula $1000 \ln \alpha_{\text{quartz water}} = 3.38 \times 10^6 T^{-1} - 3.40$ was applied to calculate the $\delta^{18}O_{H_2O}$ of fluids, where T is the Kelvin temperature [116]. The average FI homogenization temperature for each stage was used to determine the $\delta^{18}O_{H_2O}$ values.

4.6. S-Pb Isotopes

The sulfide S-Pb isotope measurements were performed at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. A Delta V Plus mass spectrometer was used to analyze the S isotopic compositions of sulfides with an analytical accuracy of $\pm 2\text{‰}$. Sulfide $\delta^{34}S$ values were calculated on sulfur dioxide produced via the traditional extraction method described in [117]. The $\delta^{34}S$ results were recorded using the Canyon Diablo Troilite (CDT).

Thermal ionization mass spectrometry using an ISOPROBE-T mass spectrometer was used to analyze the Pb isotopic compositions of sulfides and granite porphyry. The accuracy for 1 μg of $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ was greater than 0.005% (2σ). The Pb isotopic analyses are reported with respect to Pb standard reference NBS-981 values, as follows: $^{206}\text{Pb}/^{204}\text{Pb} = 16.934 \pm 0.007$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.486 \pm 0.012$, and $^{208}\text{Pb}/^{204}\text{Pb} = 36.673 \pm 0.033$ [118].

5. Results

5.1. Molybdenite Re-Os Ages

Table 1 lists the results of Re and Os isotope compositions of two molybdenite samples from the Lower Urgen deposit. The ^{187}Re and ^{187}Os contents of the samples vary from 19,468 to 27,503 ppb and 47,958 to 64,540 ppb, respectively. The Re contents of the samples are 31,202–43,934 ppb. The two Re-Os model ages are 141.2 ± 1.5 and 147.7 ± 1.7 Ma.

Table 1. Re–Os isotopic data for molybdenite from the Lower Urgen molybdenum deposit.

Sample No.	Re (ppb)		Os (ppb)		^{187}Re (ppb)		^{187}Os (ppb)		Model Age (Ma)	
	Re	1σ	Os	1σ	^{187}Re	1σ	^{187}Os	1σ	Age	1σ
G5	43,934	1558	0.083	0.008	27,503	975	64,540	0.698	141.2	1.5
LE-1	31,202	528	0.128	0.015	19,468	231	47,958	0.523	147.7	1.7

5.2. FI Petrography

Primary and secondary FIs were identified based on the criteria suggested by [109,119]. All descriptions strictly follow the concept of FIAs [109]. An FIA only applies to FI vacuoles that developed along the identical growth bands in an individual crystal, as well as within the same T-P circumstances. Nonetheless, extremely few FIs are dispersed within or along the growth bands, and the bulk is too small to be quantified ($<5 \mu\text{m}$). Most FIs that are suitable for measurement appear as isolated, clustered, or randomly distributed (Figure 5). As suggested by [109,119–121], FIs that are away from apparent cracks and appear as isolated, clustered, or randomly distributed forms are considered as primary FIs, and these FIs are selected for further investigation. In contrast, FIs along healed fractures that have apparent secondary causes are not considered. Four different types of FIs are recognized

based on phase components at room temperature and phase changes due to variations in temperature, including the two-phase (L + V) liquid-rich (L-type), saline (S-type), CO₂-rich (C1-type), and CO₂-bearing (C2-type) FIs. The descriptions of the petrographic features of each FI type are as follows.

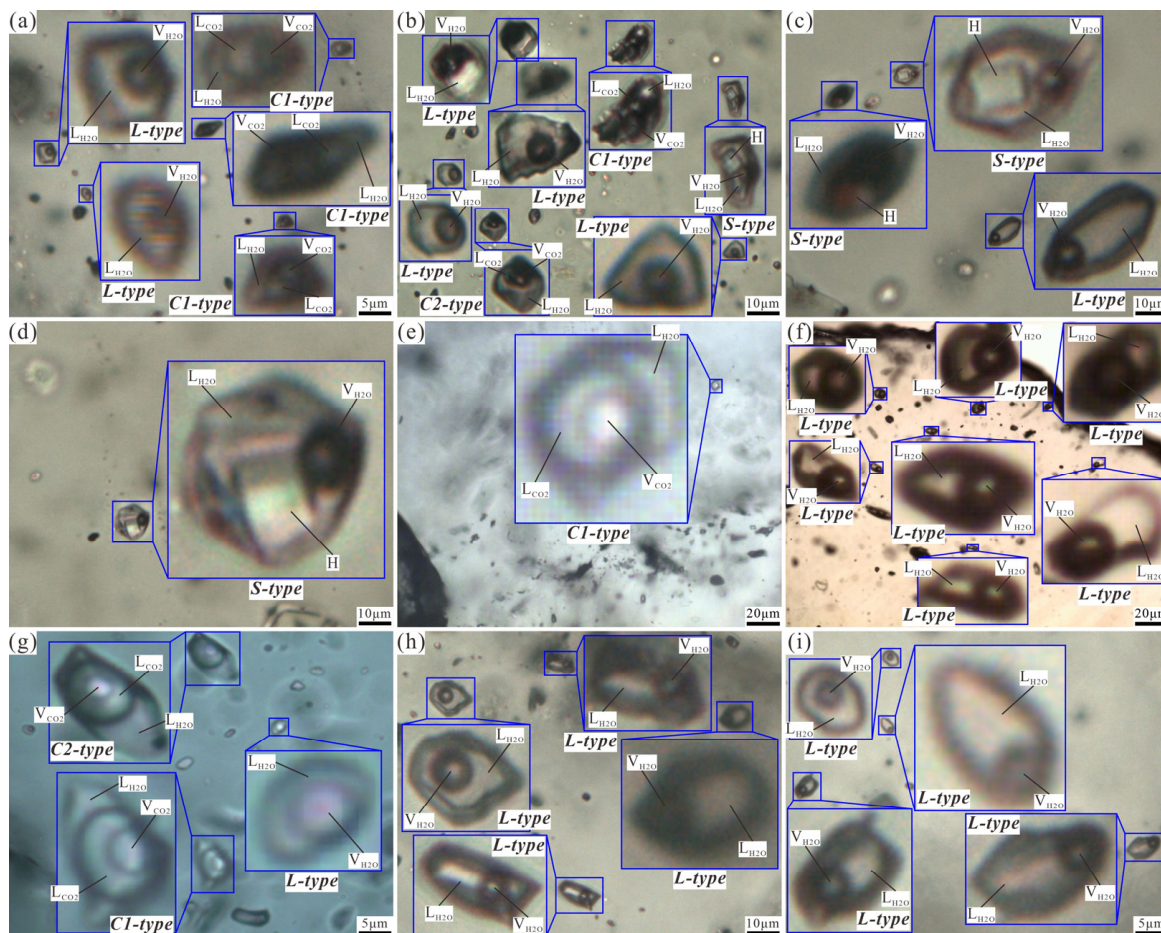


Figure 5. Representative photomicrographs of FIs in quartz veins of different stages at Lower Urgan. (a) Phase separation recorded by L- and C1-type FIs at stage 1. (b) An immiscibility FIA consisting of L-, S-, C1-, and C2-type FIs at stage 1. (c) Coexistence of L- and S-type FIs at stage 1. (d) Isolate S-type FI at stage 1. (e) Isolate C1-type FI at stage 1. (f) An FIA containing many primary L-type FIs at stage 1. (g) Phase separation recorded by L-, C1-, and C2-type FIs at stage 2. (h) An FIA containing many primary L-type FIs at stage 2. (i) An FIA containing four L-type FIs at stage 3. Abbreviations: H, halite; L_{CO2}, liquid CO₂; V_{CO2}, vapor CO₂; L_{H2O}, liquid H₂O; V_{H2O}, vapor H₂O.

L-type FIs are ubiquitous in all stages of quartz. At room temperature, they have a vapor phase and a liquid phase with L_{H2O}/(L_{H2O} + V_{H2O}) ratios of 65–90 vol% (Figure 5). With diameters ranging from 5 to 15 µm, these FIs can be ellipsoidal, rectangular, negative-crystal, or irregular in shape. L-type FIs occur alongside S-, C1-, and C2-type FIs in stage 1 as immiscibility FIAs (Figure 5a–c). They are also intergrown with C1- and C2-type FIs and form immiscibility FIAs in stage 2 quartz crystals (Figure 5g). In quartz veins of stages 1 and 2, L-type FIs are abundant and make up around 50% of all FIs; however, stage 3 veins solely contain L-type FIs.

Only stage 1 quartz veins have S-type FIs, which exhibit high salinities and densities. S-type FIs are composed of a cubic halite daughter mineral, a liquid phase, and a vapor bubble (3–10 vol%). They are elliptical, negative-crystal, or irregular in shape, with diameters of 7 to 15 µm. S-type FIs can exist alone or with L-, C1-, and C2-type FIs to form immiscibility

FIs in stage 1 (Figure 5b–d). In abundance, S-type FIs account for about 10% of all FIs in stage 1 veins.

C1-type FIs occur as ellipsoidal, circular, or negative-crystal shapes, and have a diameter of 5 to 13 μm . The CO_2 phase content ranges from 60 to 85 vol%. Usually, 60 to 80 vol% of the entire CO_2 phase is made up of vapor CO_2 . C1-type FIs commonly appear in the three-phase form ($\text{V}_{\text{CO}_2} + \text{L}_{\text{CO}_2} + \text{L}_{\text{H}_2\text{O}}$), with a small amount of the two-phase form ($\text{V}_{\text{CO}_2} + \text{L}_{\text{H}_2\text{O}}$) (Figure 5a,b,e,g). The two-phase FIs are regarded as CO_2 -rich FIs as clathrates were observed during freezing runs. In abundance, C1-type FIs frequently coexist as immiscibility FIAs with L-, S-, and C2-type FIs (Figure 5a–c,g), and account for about 25 vol% and 30 vol% of all FIAs in veins of stages 1 and 2, respectively.

At room temperature, C2-type FIs exist in the three-phase ($\text{V}_{\text{CO}_2} + \text{L}_{\text{CO}_2} + \text{L}_{\text{H}_2\text{O}}$) state, and minor FIs display a two-phase ($\text{V}_{\text{CO}_2} + \text{L}_{\text{H}_2\text{O}}$) form (Figure 5b,g). During freezing, clathrates are also observed in these two-phase C2-type FIs and can therefore be distinguished from L-type FIs. Typically, vapor CO_2 makes about 60–80 vol% of the total CO_2 phase, and the amount of CO_2 phase varies from 15 to 45 vol%. These FIs are irregular or nearly ellipsoidal in shape with a diameter of 5–15 μm . C2-type FIs are intergrown with L- and C1-type FIs (Figure 5g), together with small quantities of S-type FIs (Figure 5b), and account for approximately 15 vol% and 20 vol% of all FIAs in veins of stages 1 and 2, respectively.

5.3. FI Laser Raman Spectroscopy

Figure 6 illustrates the components of typical FIs from quartz veins of all stages. A substantial volume of H_2O and a negligible amount of CO_2 (1385 cm^{-1} , 1283 and 1388 cm^{-1} , respectively) were detected in both the liquid and vapor phase in L-type FIs of stage 1 (Figure 6a). C1-type FIs of stage 1 contain CO_2 as the only species in both the vapor and liquid CO_2 phases (1284 and 1388 cm^{-1} , 1282 and 1386 cm^{-1} , respectively) (Figure 6b). C2-type FIs of stage 1 have a similar vapor and liquid phase composition to stage 1 C1-type FIs, with CO_2 as the only component of the CO_2 phase (1283 and 1388 cm^{-1} , 1281 and 1386 cm^{-1} , respectively) (Figure 6c). Analogous liquid and vapor phase components, which are predominately made of H_2O and include a little amount of CO_2 (1385 cm^{-1} , 1284 and 1388 cm^{-1} , respectively), are present in S-type FIs of stage 1 (Figure 6d). Consequently, a $\text{NaCl-H}_2\text{O-CO}_2$ system is represented by the fluids in the quartz–molybdenite(–pyrite) stage. C1-type FIs of stage 2 show typical CO_2 spectra (1282 and 1387 cm^{-1}) in the vapor CO_2 phase (Figure 6e). The compositions of the vapor and liquid CO_2 phase of C2-type FIs in stage 2 only contain CO_2 (1281 and 1386 cm^{-1}) (Figure 6f). H_2O is the predominant gas species in the vapor phase of L-type FIs in stage 2 quartz, with only trace amounts of CO_2 (1387 cm^{-1}). In contrast, only H_2O was detected in the liquid phase of L-type FIs in stage 2 quartz (Figure 6g). Thus, a $\text{NaCl-H}_2\text{O-CO}_2$ system is represented by the fluids in the quartz–polymetallic sulfide stage. L-type FIs of stage 3 lack CO_2 detection and only have H_2O for the compositions of the liquid and vapor phases, demonstrating the characteristic of a $\text{NaCl-H}_2\text{O}$ system (Figure 6h).

5.4. FI Microthermometry

Only primary FIs were chosen for microthermometry to prevent interpretation errors brought by the post-ore modification. Using the FIA concept, the reliability of microthermometric results has been assessed [109]. Large disparities in homogenization temperatures in spatially close FIs prevent them from being unequivocally classified as an FIA; instead, they are thought to be the result of necking, stretching, or heterogeneous entrapment [120]. The microthermometry data for isolated FIs are considered, barring a significant discrepancy with surrounding FIs [121]. If the homogenization temperature variation within a cluster of a single FI type is below $15\text{ }^\circ\text{C}$, the possibility of post-entrapment modification, generational overlap, or heterogeneous trapping of FIs is ruled out, and it is argued that these FIs represent a uniform fluid entrapment. We thus suggest that those results are trustworthy and that the overall average of a cluster is adequate for additional research [120]. An immiscibility FIA is a group of FIs of various types that possess comparable ranges of ho-

mogenization temperature (variation below 15 °C) but distinct homogenization processes. In this case, the complete FIA was represented for statistical analysis by the average of several types of FIs.

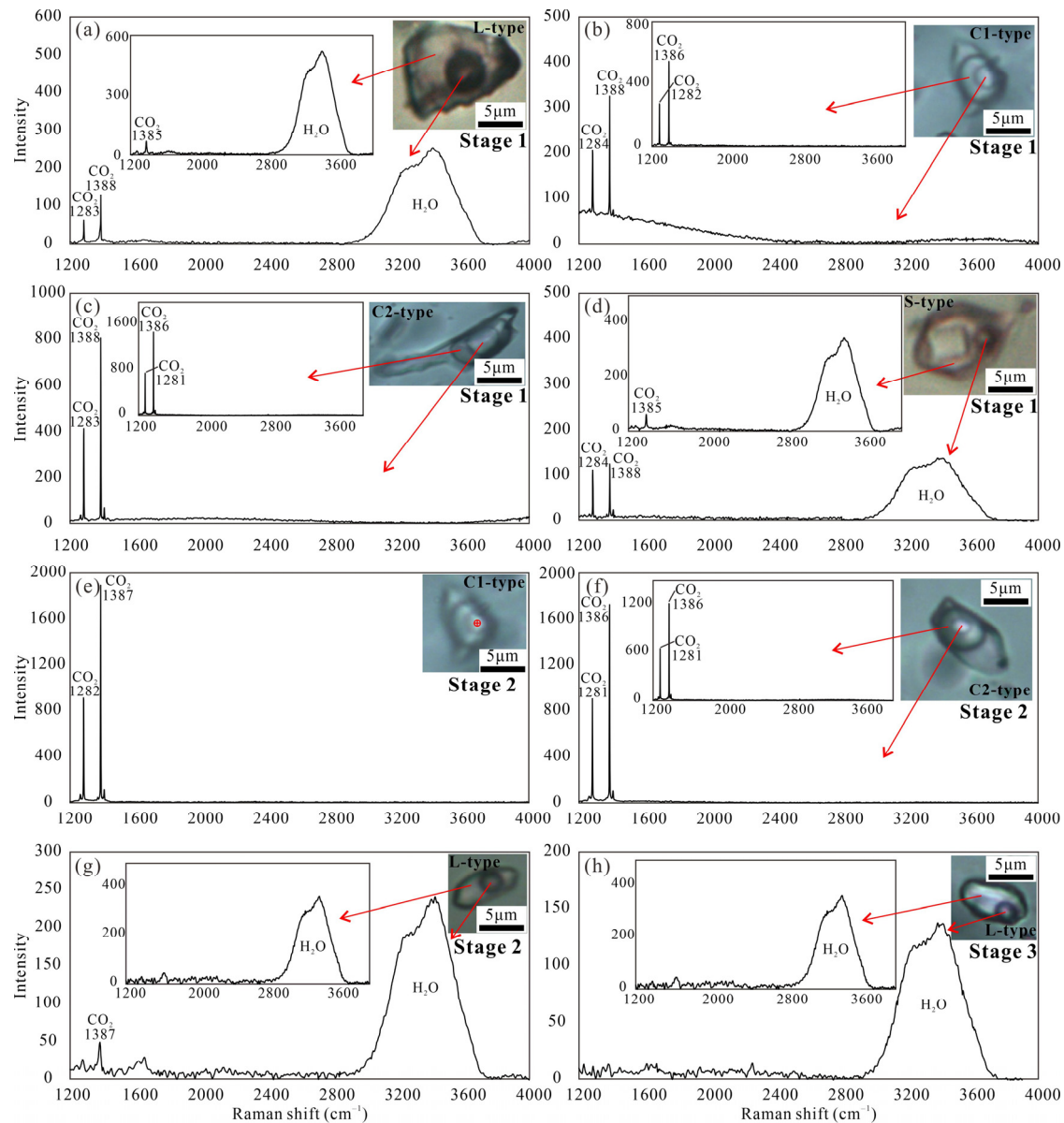


Figure 6. Representative laser Raman spectra for FIs from the Lower Urgen molybdenum deposit. (a) Raman spectra of stage 1 L-type FI reflect the presence of H₂O and minor amounts of CO₂. (b) Raman spectra of stage 1 C1-type FI indicate the presence of CO₂ in the CO₂ phase (V_{CO₂} + L_{CO₂}). (c) Raman spectra of stage 1 C2-type FI reflect the existence of CO₂ in the CO₂ phase (V_{CO₂} + L_{CO₂}). (d) Raman spectra of stage 1 S-type FI indicate the presence of H₂O and minor amounts of CO₂. (e) Raman spectra of stage 2 C1-type FI reflect the occurrence of CO₂ in vapor CO₂. (f) Raman spectra of stage 2 C2-type FI indicate the existence of CO₂ in the CO₂ phase (V_{CO₂} + L_{CO₂}). (g) Raman spectra of stage 2 L-type FI reflect the presence of H₂O and minor amounts of CO₂. (h) Raman spectra of stage 3 L-type FI indicate the existence of H₂O.

In this investigation, microthermometric results for 320 FIAs of three stages are listed in Table S1 (see the Supplementary Materials) and illustrated in Figure 7. The T_{fm_ice} for L-type FIs of all stages ranges from −21.6 to −20.8 °C, consistent with the eutectic temperature of the H₂O–NaCl system, indicating that most of the dissolved salts are

NaCl [111,122]. As mentioned in Section 5.3, the L- and S-type FIs sometimes display weak CO₂ signals, but the CO₂ characteristics cannot be observed during the petrography observation and microthermometry of these FIs. The detection limit of CO₂ through laser Raman spectroscopy can be as low as 1 bar, while the phase transition of CO₂ can be observed in microthermometry with a CO₂ pressure of at least 10.4 bar (the melting of CO₂ clathrate can be observed) or 45 bar (solid phase of CO₂ melting can be observed) [123]. In summary, the amount of CO₂ in the S-type FIs of stage 1 and L-type FIs of stages 1 and 2 is extremely low and almost negligible, and thus the salinities of these FIs were obtained using the T_{mH} and T_{mice} , respectively.

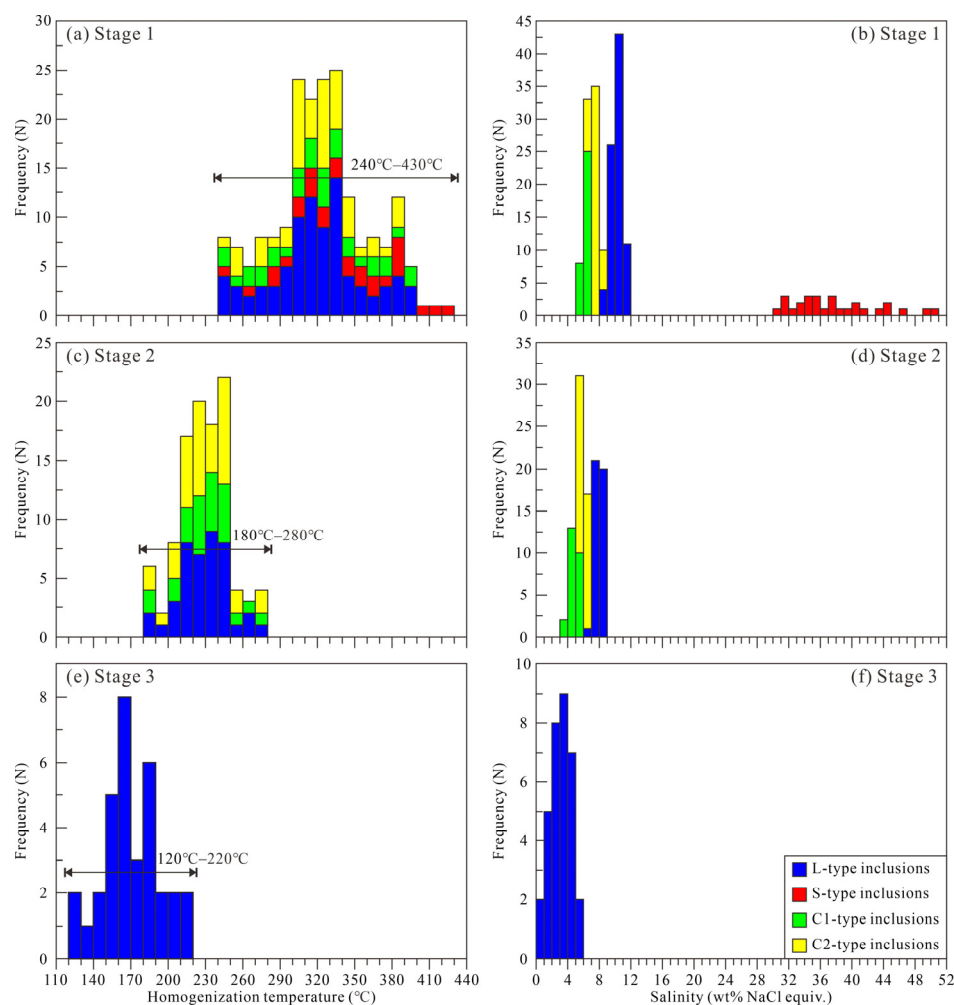


Figure 7. Histograms of homogenization temperatures (a,c,e) and salinities (b,d,f) for FIs in quartz from the Lower Urgan molybdenum deposit according to the concept of FIAs.

The entrapped fluid characteristics are often dramatically changed through post-entrapment modification (dismemberment and/or migration) in quartz-hosted FIs [124,125]. Euhedral quartz crystals that are naturally formed frequently exhibit these modifications in addition to quartz phenocrysts and veins. Although not verified, a satisfactory FI preservation state is recommended if the FIs display constant phase ratios, develop in clear trails or growth bands, and provide densely concentrated microthermometric values [125]. On the contrary, regular negative-crystal forms are neither necessary nor indicative of the preservation of syn-entrapment characteristics of FIs. Unless they adhere to specified growth bands, clusters of randomly scattered FIs often reflect secondary or pseudosecondary FI trails that have dissolved. Audétat [124] demonstrated that the decline in FI volume caused by post-entrapment modification results in a decrease in the homogenization temperature,

a steepening of the isochore, and an increase in fluid density. By contrast, in magmatic–hydrothermal systems, water loss from FIs seldom surpasses twenty percent; consequently, the fluid salinities that are determined should, in most instances, be almost accurate. In the current research, FIs inside or along the growth zones of euhedral quartz occur incredibly seldom, and the bulk of them are too small to investigate ($<5\ \mu\text{m}$). Post-entrapment modification may have occurred to varied degrees in clustered, isolated, and randomly dispersed FIs, but it seems inescapable. However, to guarantee that the chosen FIAs only had slight effects of post-entrapment modification, FIAs that displayed obvious post-entrapment modification features, e.g., deformation, movement tracks, stretching, shrinkage, or deteriorating halos, have been excluded [119,124–126]. Nonetheless, the genuine densities and homogenization temperatures of the examined FIs are slightly lower and higher than the calculated data, respectively. Comparatively, FI salinities are frequently less influenced, and most of them tend to have maintained their original salinities. As a result, we primarily concentrate on the salinities of the examined FIs, while the homogenization temperatures are used as a reference.

Stage 1 veins contain L-, S-, C1-, and C2-type FIs. The Th of L-type FIs ranges from 240 to 400 °C, and the $T_{m_{ice}}$ varies between -8.2 and -5.1 °C (corresponding to 8.0–11.9 wt% NaCl equiv.). The disappearance of the vapor bubbles indicates complete homogenization. The T_{m_H} of S-type FIs is between 160 and 428 °C (corresponding to 30.1–50.8 wt% NaCl equiv.). Halite dissolution or the disappearance of vapor bubbles is an indicator that S-type FIs homogenize between 245 and 428 °C. The $T_{m_{CO_2}}$ of C1-type FIs ranges from -59.8 to -57.0 °C. C1-type FIs have a $T_{m_{clath}}$ of 5.9–7.4 °C and calculated salinities of 5.0–7.5 wt% NaCl equiv. At 14.5–21.5 °C, the CO_2 phase homogenizes to the vapor CO_2 phase. At 240–397 °C, the liquid H_2O phase disappears, signifying the completion of the homogenization. C2-type FIs have a $T_{m_{CO_2}}$ of -59.8 to -57.0 °C and $T_{m_{clath}}$ of 5.1–6.8 °C, corresponding to salinities of 6.0–8.8 wt% NaCl equiv. At 20.3–25.9 °C, CO_2 homogenizes to the vapor CO_2 phase, and at 241–395 °C, C2-type FIs finally homogenize to the liquid phase (Figure 7a,b).

L-, C1-, and C2-type FIs can be found in stage 2 quartz veins. Compared to stage 1 FIs, these FIs have a lower Th and lower salinities (Figure 7c,d). L-type FIs have a $T_{m_{ice}}$ of -5.9 to -3.7 °C, corresponding to 6.0–9.1 wt% NaCl equiv. At 182–278 °C, L-type FIs homogenize and are characterized by the vapor bubbles' disappearance. C1-type FIs yield a $T_{m_{CO_2}}$ of -59.8 to -57.0 °C, $T_{m_{clath}}$ of 6.8–8.5 °C, and calculated salinities of 3.0–6.0 wt% NaCl equiv. At 14.6–22.5 °C, the CO_2 phase homogenizes to the vapor CO_2 phase, and at 181–277 °C, the liquid H_2O phase is eliminated, indicating complete homogenization. C2-type FIs contain a $T_{m_{CO_2}}$ that varies between -59.8 and -56.8 °C and a $T_{m_{clath}}$ of 6.2–7.9 °C (corresponding to 4.1–7.1 wt% NaCl equiv.). The homogeneity of the CO_2 phase is featured by the elimination of the liquid CO_2 phase, and the Th_{CO_2} has a range of 21.9–25.9 °C. Total homogenization occurs when the vapor CO_2 phase is eliminated, and the Th of C2-type FIs has a range of 180–277 °C (Figure 7c,d).

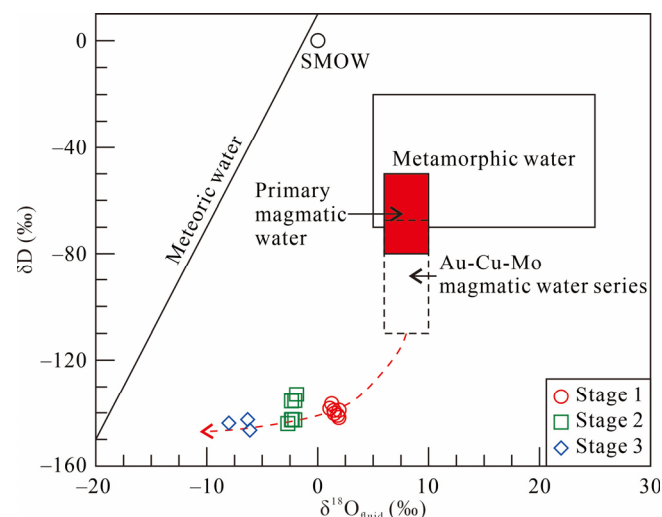
L-type FIs are the only FIs found in quartz–carbonate veins of stage 3, which have $T_{m_{ice}}$ values between -5.0 and -0.1 °C and NaCl equivalent salinities between 0.2 and 7.9 wt%. At 120–218 °C, these FIs ultimately homogenize to the liquid phase (Figure 7e,f).

5.5. Quartz H-O Isotopic Compositions

The hydrogen and oxygen isotopic compositions of analyzed quartz samples are presented in Table 2 and shown in Figure 8. Seven quartz samples of stage 1 veins have δD and $\delta^{18}O$ values ranging from -141.8 to -136.5 ‰ and 7.2–8.0‰, respectively. The $\delta^{18}O_{fluid}$ values are determined to be between 1.1 and 1.9‰. The δD values of seven quartz samples collected from stage 2 veins are -144.1 to -129.9 ‰, the $\delta^{18}O$ values range between 7.3 and 8.1‰, and the calculated $\delta^{18}O_{fluid}$ values are -2.7 to -1.9 ‰. The δD and $\delta^{18}O$ values in three quartz samples from stage 3 veins are -146.6 to -142.6 ‰ and 5.8–7.7‰, respectively, and the calculated $\delta^{18}O_{fluid}$ values are between -8.0 and -6.1 ‰.

Table 2. Hydrogen and oxygen isotopic compositions of quartz from the Lower Urgan molybdenum deposit.

Sample No.	Stage	Mineral	δD (‰)	$\delta^{18}O_{\text{quartz}}$ (‰)	T (°C)	$\delta^{18}O_{\text{fluid}}$ (‰)
B16-1	Stage 1	Quartz	−140.2	7.6	323	1.5
B16-2	Stage 1	Quartz	−138.3	7.2	323	1.1
B16-3	Stage 1	Quartz	−136.5	7.4	323	1.3
B16-4	Stage 1	Quartz	−140.9	7.9	323	1.8
B16-5	Stage 1	Quartz	−139.0	8.0	323	1.9
B16-6	Stage 1	Quartz	−141.8	8.0	323	1.9
B16-7	Stage 1	Quartz	−139.1	7.6	323	1.5
D14-1	Stage 2	Quartz	−142.7	7.9	229	−2.1
D16-1	Stage 2	Quartz	−135.5	7.6	229	−2.4
D16-4	Stage 2	Quartz	−142.5	7.7	229	−2.3
D16-6	Stage 2	Quartz	−135.4	7.9	229	−2.1
D16-7	Stage 2	Quartz	−129.9	8.1	229	−1.9
D16-8	Stage 2	Quartz	−142.7	7.6	229	−2.4
D16-9	Stage 2	Quartz	−144.1	7.3	229	−2.7
G8-1	Stage 3	Quartz	−146.6	7.7	170	−6.1
G10-1	Stage 3	Quartz	−143.9	5.8	170	−8.0
G11-1	Stage 3	Quartz	−142.6	7.5	170	−6.3

**Figure 8.** δD versus $\delta^{18}O_{\text{fluid}}$ diagram for the Lower Urgan molybdenum deposit (base map after [127]). The magmatic water field of the Au-Cu-Mo series is from [128].

5.6. Sulfide S Isotopic Compositions

In Table 3 and Figure 9, the S isotopic compositions of molybdenite, pyrite, chalcopyrite, and galena collected from the Lower Urgan molybdenum deposit are displayed. Sulfide $\delta^{34}S$ values range from 3.9 to 5.5‰, with an average value of 5.2‰. Six molybdenite samples contain $\delta^{34}S$ values of 5.4–5.5‰. Two pyrite samples and two chalcopyrite samples have $\delta^{34}S$ values of 5.4‰ and 4.8–5.4‰, respectively. One galena sample has a $\delta^{34}S$ value of 3.9‰.

Table 3. Sulfur isotopic compositions of sulfides from the Lower Urgan molybdenum deposit.

Sample No.	Stage	Mineral	$\delta^{34}S$ (‰)
LU16-1	Stage 1	Molybdenite	5.5
LU16-2	Stage 1	Molybdenite	5.4
LU16-3	Stage 1	Molybdenite	5.5

Table 3. Cont.

Sample No.	Stage	Mineral	$\delta^{34}\text{S}$ (‰)
LU16-4	Stage 1	Molybdenite	5.5
LU16-5	Stage 1	Molybdenite	5.5
LU16-6	Stage 1	Molybdenite	5.5
LU16-7	Stage 2	Pyrite	5.4
LU16-8	Stage 2	Pyrite	5.4
LU16-9	Stage 2	Chalcopyrite	5.4
LU16-10	Stage 2	Chalcopyrite	4.8
LU16-11	Stage 2	Galena	3.9

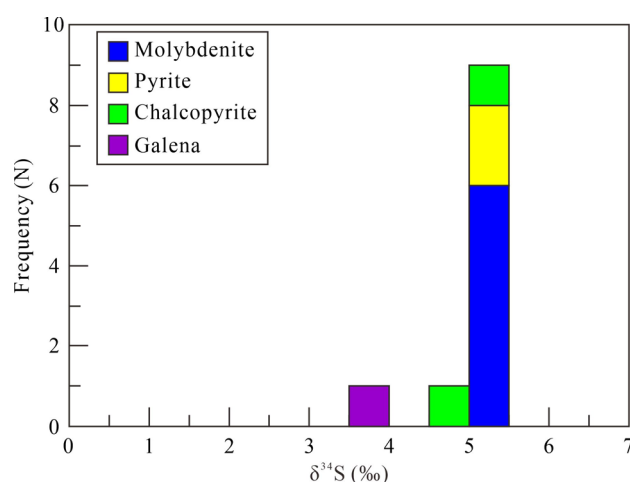


Figure 9. Histogram of sulfur isotopic compositions of metal sulfides from the Lower Urgen molybdenum deposit.

5.7. Sulfides and Whole-Rock Pb Isotopic Compositions

The Pb isotopic compositions of molybdenite, pyrite, chalcopyrite, galena, and granite porphyry are given in Table 4 and Figure 10. The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios for eight molybdenite samples are 18.340–18.412, 15.540–15.546, and 38.130–38.212, respectively. Five pyrite samples contain $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of 18.336–18.510, 15.542–15.569, and 38.131–38.312, respectively. The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of two chalcopyrite samples are 18.336–18.340, 15.541–15.547, and 38.131–38.143, respectively. One galena sample has $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of 18.343, 15.550, and 38.149, respectively. The $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of three molybdenum-bearing granite porphyry samples range from 18.535 to 18.599, 15.571 to 15.574, and 38.419 to 38.583, respectively.

Table 4. Pb isotopic composition of sulfide and granite porphyry samples from the Lower Urgen molybdenum deposit.

Sample No.	Stage	Mineral	$^{206}\text{Pb}/^{204}\text{Pb}$	2σ	$^{207}\text{Pb}/^{204}\text{Pb}$	2σ	$^{208}\text{Pb}/^{204}\text{Pb}$	2σ	μ
D17-2	1	Molybdenite	18.340	0.0004	15.542	0.0003	38.137	0.0008	9.36
D17-3	1	Molybdenite	18.340	0.0005	15.543	0.0005	38.153	0.0011	9.36
D17-4	1	Molybdenite	18.355	0.0004	15.544	0.0004	38.164	0.0009	9.36
D17-5	1	Molybdenite	18.343	0.0004	15.540	0.0004	38.135	0.0009	9.35
D17-7	1	Molybdenite	18.340	0.0004	15.540	0.0004	38.130	0.0009	9.35
D0A1-1	1	Molybdenite	18.412	0.0004	15.546	0.0004	38.212	0.0009	9.36
D0A1-2	1	Molybdenite	18.387	0.0004	15.544	0.0004	38.183	0.0010	9.36
D0a1-1	1	Molybdenite	18.363	0.0004	15.543	0.0003	38.170	0.0009	9.36

Table 4. Cont.

Sample No.	Stage	Mineral	$^{206}\text{Pb}/^{204}\text{Pb}$	2σ	$^{207}\text{Pb}/^{204}\text{Pb}$	2σ	$^{208}\text{Pb}/^{204}\text{Pb}$	2σ	μ
G10-2	2	Pyrite	18.373	0.0005	15.549	0.0004	38.174	0.0010	9.37
G11-2	2	Pyrite	18.510	0.0004	15.557	0.0004	38.249	0.0010	9.37
G13	2	Pyrite	18.471	0.0004	15.569	0.0003	38.312	0.0008	9.40
G14	2	Pyrite	18.341	0.0003	15.549	0.0003	38.148	0.0008	9.37
D17-1	2	Pyrite	18.336	0.0003	15.542	0.0002	38.131	0.0006	9.36
D17-2	2	Chalcopyrite	18.336	0.0005	15.541	0.0004	38.131	0.0011	9.36
G8-2	2	Chalcopyrite	18.340	0.0004	15.547	0.0003	38.143	0.0008	9.37
G8-3	2	Galena	18.343	0.0004	15.550	0.0004	38.149	0.0009	9.37
T0a1-1	–	Granite porphyry	18.599	0.0005	15.574	0.0005	38.583	0.0013	9.40
T0a1-2	–	Granite porphyry	18.565	0.0005	15.573	0.0004	38.515	0.0012	9.40
T16-1	–	Granite porphyry	18.535	0.0004	15.571	0.0004	38.419	0.0010	9.39

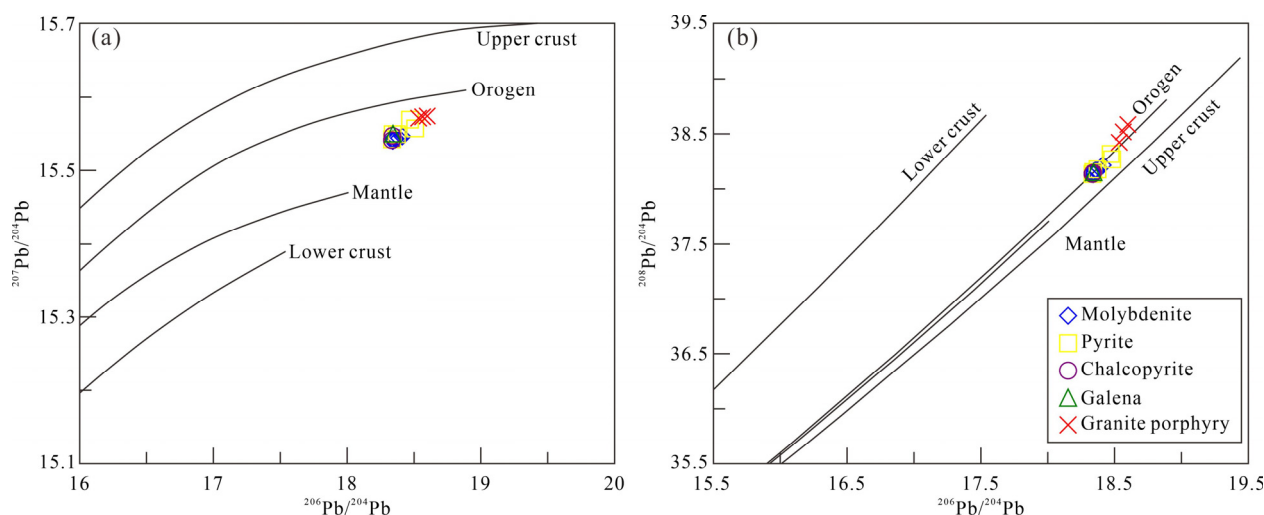


Figure 10. (a) $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ diagram. (b) $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ diagram (modified from [129]).

6. Discussion

6.1. Timing of Molybdenum Metallogenesis

From both scientific and economic perspectives, it is crucial to constrain the length and time of magmatic–hydrothermal systems [130]. Precise isotopic dating of hydrothermal minerals is an essential technique for determining the geochronology of hydrothermal processes in relation to intrusive magmatism and for constructing genetic models of hydrothermal deposits. As the primary product of hydrothermal mineralization, molybdenite obtained from ore-bearing quartz veins in molybdenum deposits is suggested as a Re–Os geochronometer for directly dating molybdenum mineralization events. In this contribution, two Re–Os model ages of 141.2 ± 1.5 and 147.7 ± 1.7 Ma were obtained. The wide range of Re–Os model ages could be attributed to Re and Os isotope decoupling, the considerable spatial Re heterogeneity, the post-ore deformation, and the analytical procedure [130–136]. For instance, many explanations based on post-crystallization diffusion of ^{187}Os are proposed to answer the Re and Os decoupling mechanism. ReS_2 inclusions or 3R polytype molybdenite formed during the crystallization of molybdenite would, over time, result in a chemical gradient for ^{187}Os that may homogenize during a thermal event. Decoupling could also result from the exsolution of Os-rich sulfides or diffusion of Os to crystal dislocations within the molybdenite during metamorphism [133,134]. The heterogeneous distribution of Re in

molybdenite samples could also lead to the discrepancy of Re-Os model ages, which may be related to the overall abundance of Re in the hydrothermal fluids [136], compositional changes in the hydrothermal fluid with time [132], or partitioning of Re between liquid and vapor [130]. Additionally, a relatively wide range of molybdenite Re-Os model ages has been reported in numerous magmatic–hydrothermal deposits, such as the Haigou Au deposit (311.3–306.7 Ma; [131]), Lala Fe-Cu deposit (1097–1081 Ma; [137]), Kenge Mo deposit (1957–1950 Ma; [138]), Porcupine Mo deposit (1896–1882 Ma; [138]), Kedengjian Cu deposit (99.1–95.7 Ma; [139]), Mada Mo deposit (150.9–136.9 Ma; [140]), Meiziwo W deposit (165.6–156.2 Ma; [141]), Yaoling W deposit (165.9–156.2 Ma; [141]), Banlashan Mo deposit (142.7–131.8 Ma; [26]), Huashandong W deposit (827.8–795.3 Ma; [142]), Jiguanshan Mo deposit (156.2–151.7 Ma; [143]), and Dongbeigou Mo deposit (132.6–127.1 Ma; [144]). Zhang et al. [31] reported that the barren quartz monzonite porphyry and syenite porphyry stocks were emplaced at 165.0 ± 2.5 and 125.5 ± 1.9 Ma, respectively. Our recent geochronology study yielded a zircon U-Pb age of 142.3 ± 0.5 Ma for molybdenum-bearing granite porphyry stock (unpublished data). In recent decades, advances in high-precision dating, numerical simulation, and diffusion modeling mostly argue for short-lived (<1 Ma) timescales for the lifetime of magmatic–hydrothermal systems [7,145–152]. The Re-Os model age of molybdenite sample G5 (141.2 ± 1.5 Ma) is highly consistent with the emplacement time of the molybdenum-bearing granite porphyry stock within the analytical uncertainty. Spatially, the molybdenum mineralization in the deposit is characterized by veinlet-disseminated- and vein-type quartz–sulfide orebodies hosted in the cupola of the ore-bearing granite porphyry stock (Figure 2c). Geochemically, the metal sulfides obtained in this study have similar lead isotopic compositions to those of the ore-bearing granite porphyry stock (discussed in Section 6.3). This evidence collectively demonstrates that the molybdenum mineralization at Lower Urgen was temporally, spatially, and genetically associated with the molybdenum-bearing granite porphyry stock, supporting an intrusion-related origin during the Early Cretaceous. In contrast, the barren quartz monzonite porphyry and syenite porphyry stocks record pre-ore and post-ore magmatic events, respectively. Our findings also indicate that accurate and precise molybdenite Re-Os ages representing the true timing of ore formation need an integrated combination of careful geology, geochemistry, and multiple dating methods.

Considering the Mesozoic intense and widespread molybdenum mineralization in NE China, molybdenum mineralization at Lower Urgen is not a singular instance. By collecting published molybdenite Re-Os ages for Mesozoic molybdenum deposits within NE China, we determine three periods of molybdenum metallogenesis events in the region: Middle–Late Triassic (245–225 Ma), Early–Middle Jurassic (200–165 Ma), and Late Jurassic–Early Cretaceous (160–130 Ma) (Table S2 and Figure 11). The Middle–Late Triassic molybdenum deposits are primarily located in the southern GXR (SGXR) and along the SXCF, with minor occurrences in the NCGXR, including the Laojiagou (234.9 Ma; [41]), Chehugou (245 Ma; [85]), Kulitu (236 Ma; [153]), and Badaguan deposits (228.8–225.1 Ma; [46,48,154]). Molybdenum deposits formed in the Early to Middle Jurassic are abundant within the LXZR, and scattered in the NCGXR, including the Daheishan (169.2–168.0 Ma; [52,155,156]), Xingshan (167.3 Ma; [53]), Jidetun (168.9–168.0 Ma; [54,58,157]), Fu'anpu (168.2–166.9 Ma; [57,158]), Houdaomu (167.5 Ma; [159]), Shuangshan (171.6 Ma; [160]), Jiapigou (196 Ma; [160]), Sancha (183.1 Ma; [160]), Dashihe (186.7 Ma; [161]), Liushengdian (169.3–168.7 Ma; [159,162]), Sifangdianzi (176.6 Ma; [59]), Luming (177.9–176.7 Ma; [61,62]), Huojihe (181.3 Ma; [64]), Xinhualong (171.3 Ma; [159]), Wunugetushan (180.5–177.6 Ma; [49,163]), and Taipingchuan deposits (200.1 Ma; [164]). Most of the molybdenum deposits dated between the Late Jurassic and Early Cretaceous are located in the GXR, including the Chalukou (150–148 Ma; [65,67]), Taipinggou (130.1–129.4 Ma; [72,165]), Jiazishan (147.4 Ma; [166]), Diyanqinamu (156.2 Ma; [167]), Hashitu (150 Ma; [75]), Aolunhua (132–129.4 Ma; [79,168,169]), Shabutai (135.3 Ma; [26]), Haisugou (136.4 Ma; [26]), Banlashan (143–136.1 Ma; [26,169]), Yangchang (138.5 Ma; [169]), Hongshanzi (138.2–137.2 Ma; [83]), Xiaodonggou (138.1–135.5 Ma; [84,170]), Nianzigou (154.3–153 Ma; [85,86,153]), and Jiguanshan deposits (155.4–151.1 Ma; [143,171]). The zircon

U-Pb ages of ore-bearing granodiorites record the granitic magmatism in the Kanchuangou and Jinchanggou deposits at 111.1 [56] and 114 Ma [63], respectively. Unfortunately, no accurate molybdenite Re-Os ages of these two deposits have been reported, and the genetic relationship between molybdenum mineralization and host granodiorites remains to be further investigated. Hence, the molybdenum mineralization in these two deposits is not involved in the present study. The Early Cretaceous molybdenum mineralization in Lower Urgen is in accordance with the Late Jurassic–Early Cretaceous molybdenum metallogenesis in the NCGXR.

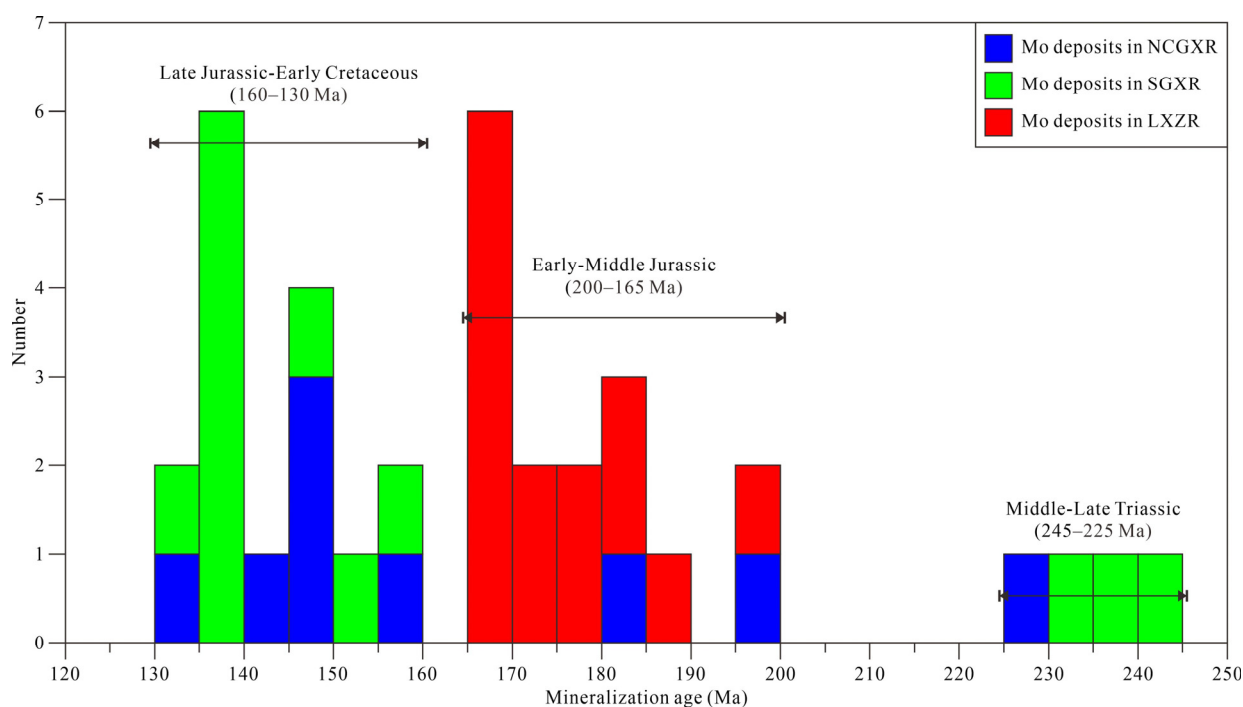


Figure 11. Histogram of molybdenite Re-Os isochron ages for Mesozoic molybdenum deposits in NE China. Abbreviations: NCGXR, northern and central Great Xing’an Range; SGXR, southern Great Xing’an Range; LXZR, lesser Xing’an-Zhangguangcai Range. Data sources are listed in Table S2.

6.2. Source of Mineralizing Fluids

Stage 1 quartz has calculated $\delta^{18}\text{O}_{\text{fluid}}$ values (1.1 to 1.9‰) that are lower than normal magmatic fluids (7–9‰; [172]) and substantially higher than normal Mesozoic meteoric water (−18‰; [173]). The $\delta^{18}\text{O}_{\text{fluid}}$ values of the quartz samples from the late quartz–carbonate stage are more depleted (−8.0 to −6.1‰) and comparable to the values of Mesozoic meteoric water [127,173] (Figure 8). This $\delta^{18}\text{O}_{\text{fluid}}$ variation trend implies the mixing of magmatic fluids with later meteoric water during the mineralization at Lower Urgen. Furthermore, in agreement with the documented δD values of Mesozoic meteoric water in the GXR (−140 to −90‰; [173]), the δD values of all stages (−146.6 to −129.9‰) are much lower than those of magmatic water (−50 to −85‰; [174]). The depletion of δD in the mineralizing fluids could be controlled through (1) fluid boiling or immiscibility [175], (2) magma degassing led by major meteoric water incursion [176], and (3) hydrogen isotope fractionation between the mineralizing fluids and some reduced species (e.g., CH_4). As shown in Figure 5, the coexistence of multiple FI types in stages 1 and 2 indicates intense fluid immiscibility during ore precipitation. The decreasing trend of Th and salinity in the FIs from stage 1 to 3 indicates increasing meteoric water input toward the late fluid system (Figure 7). However, no reduced species such as CH_4 have been detected in the H_2O -dominated ore-forming fluids, which indicates that hydrogen isotope fractionation is likely negligible [127]. Hence, we preliminarily speculate that fluid immiscibility and meteoric water input could explain the δD depletion of ore-forming fluids at Lower Urgen. In the δD versus $\delta^{18}\text{O}_{\text{fluid}}$ diagram, the calculated $\delta^{18}\text{O}_{\text{fluid}}$ and δD values also show a clear

evolution trend from stage 1 to 3, and the data are plotted between the magmatic and meteoric water fields (Figure 8). Therefore, we conclude that the mineralizing fluids of the Lower Urgen deposit were primarily of magmatic origin with progressive meteoric water input.

6.3. Source of Sulfur and Lead

S isotopes can be used to trace the source of sulfur in sulfide minerals, despite the fact that the entire S isotopic components could be influenced by pH, temperature, ion activity, and f_{O_2} [177–179]. The $\delta^{34}S$ data of sulfides can be utilized to determine their origin because no sulfate minerals have been found in the Lower Urgen district. The molybdenite, pyrite, chalcopyrite, and galena have $\delta^{34}S$ values of 5.4–5.5‰, 5.4‰, 4.8–5.4‰, and 3.9‰, respectively, implying that these sulfides have reached sulfide equilibrium fractionation [179]. The sulfides $\delta^{34}S$ values of the Lower Urgen deposit display a restricted range (3.9–5.5‰), which is commonly interpreted as a magma-derived sulfur [180] (Figure 9).

The source of the lead in the mineralizing fluids has been constrained using the lead isotope ratios of sulfides. The Pb isotopic ratios of sulfides can provide information about the source of Pb since sulfide minerals often have minimal radiogenic Pb isotopes and extremely low quantities of Th and U [129,181]. By contrasting the Pb isotope ratios of molybdenite, pyrite, chalcopyrite, galena, and molybdenum-bearing granite porphyry, the Pb source of the Lower Urgen molybdenum deposit can be determined. The sulfide samples have narrow ranges of $^{206}Pb/^{204}Pb$ (18.336–18.510), $^{207}Pb/^{204}Pb$ (15.540–15.569), and $^{208}Pb/^{204}Pb$ (38.130–38.312), implying an individual or successfully mixed lead origin. The Pb isotopic ratios of sulfides in the Lower Urgen deposit are distinct from those of the surrounding Mesozoic strata (e.g., Tamulagou and Manketouebo Fms) ($^{206}Pb/^{204}Pb$ = 18.08–18.32, $^{207}Pb/^{204}Pb$ = 15.46–15.55, and $^{208}Pb/^{204}Pb$ = 37.62–38.10) [93,182], but similar to those of the ore-bearing granite porphyry stock in the deposit ($^{206}Pb/^{204}Pb$ = 18.535–18.599, $^{207}Pb/^{204}Pb$ = 15.571–15.574, and $^{208}Pb/^{204}Pb$ = 38.419–38.583). Lead with high μ values (>9.58) was derived from the upper crust [129], whereas that with values of 8.92 was derived from the mantle [183]. The sulfides and granite porphyry stock from the Lower Urgen deposit yield μ values of 9.35–9.40 and 9.39–9.40, respectively, indicating that lead was basically from the crustal source and an extremely small amount of the mantle source. On the diagram of $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ [129], the sulfide and ore-bearing granite porphyry samples are all located between the mantle and orogen evolution curves (Figure 10a). On the diagram of $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ [129], most sulfide and ore-bearing granite porphyry samples are distributed on the orogen evolution curve (Figure 10b). These features imply that the metal sulfides and granite porphyry at Lower Urgen have the same lead source, which has been documented in many porphyry deposits [2,3,184], and that the granitic magmatism is probably largely responsible for the molybdenum mineralization in the Lower Urgen deposit.

6.4. Metal Precipitation Mechanisms

Fluid immiscibility, one of the most significant ore-forming mechanisms in magmatic–hydrothermal metallogenic systems, can change the temperature, pH, and salinity of the ore-bearing fluids, thereby reducing the solubility of metals in the fluids [14,185–188]. The occurrence of fluid immiscibility is supported by the following evidence from stage 1 quartz-hosted FIs: (1) L-, S-, C1-, and C2-type FIs have intimate spatial relationships (Figure 5a–c); (2) they exhibit distinct homogenization modes; and (3) these FIs show distinct salinities and comparable homogenization temperature ranges (Figure 7a,b). Similarly, at stage 2, L-, C1-, and C2-type FIs frequently coexist, indicating that they were simultaneously captured and showed different homogenization modes (Figures 5g and 7c,d). Notably, in stages 1 and 2, C1- and C2-type FIs frequently show lower salinities but analogous homogenization temperatures than L-type FIs, which shows that fluid immiscibility occurred before their entrapment [189]. The increased salinity of the residual fluids caused by volatile separation from the ore-bearing fluids as temperature and pressure drops may be the cause of the

higher salinities in L-type FIs than those in C1- and C2-type FIs [185,190]. The mineralizing fluids at Lower Urgen underwent fluid immiscibility processes during stages 1 and 2, as reflected by the diagram of salinity versus homogenization temperature (Figure 12). Field evidence, such as the widespread fracture and brecciation of granite porphyry cupola and the overlying intermediate–basic volcanic rocks at Lower Urgen, suggests a dramatic pressure drop that might result in fluid immiscibility, further supporting the existence of fluid immiscibility [119,191–193]. Previous research has demonstrated that a mafic magmatic source or the magmatic–hydrothermal formation procedure of a deep-seated magma chamber often contributes significant amounts of dissolved CO_2 [119,194–198]. In combination with the H–O isotopic compositions of stage 1 quartz, we speculate that the original fluids of the Lower Urgen molybdenum deposit are CO_2 -rich magmatic–hydrothermal fluids. As the fluids rose, volatiles (such as CO_2) started to separate from the fluids due to a decrease in pressure and temperature. The sudden supersaturation of the solution was caused by the release of volatiles, which also increased the pH of the solution and caused the decoupling of metal complexes. As a result of the procedure, significant amounts of molybdenite precipitated from stage 1 fluids, while chalcopyrite, pyrite, sphalerite, arsenopyrite, and galena were deposited from stage 2 fluids.

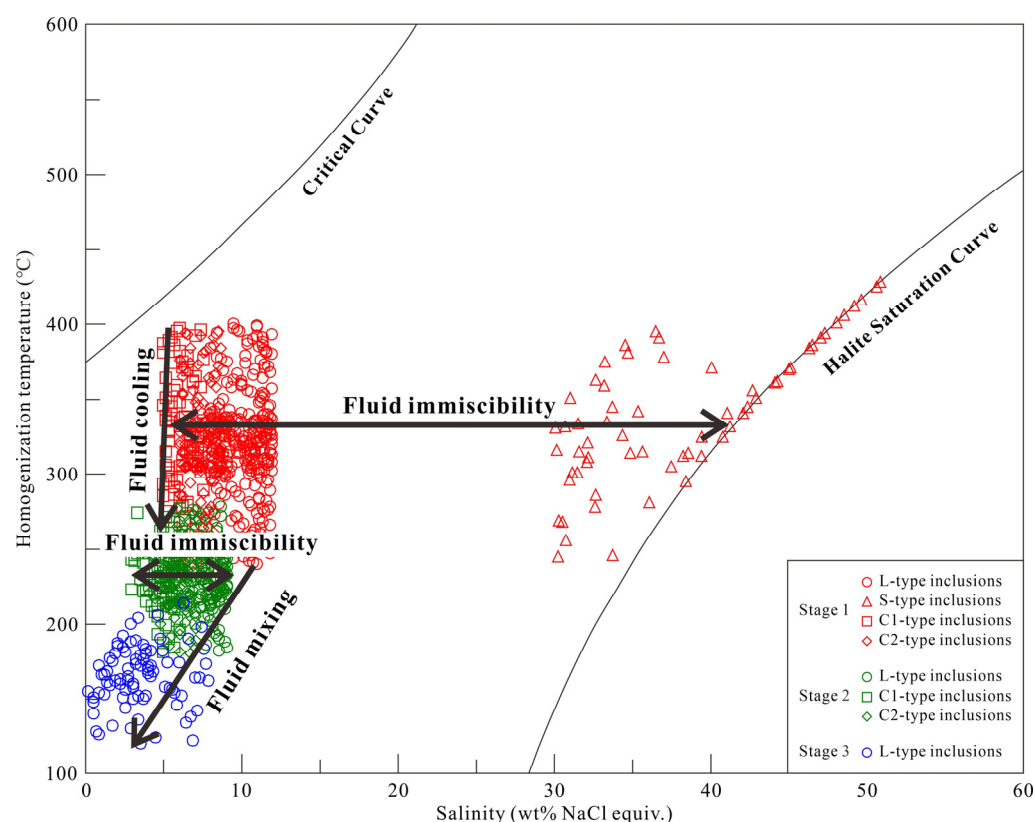
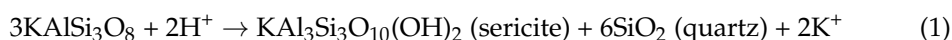


Figure 12. Homogenization temperature versus salinity of FIs from all stages in the Lower Urgen molybdenum deposit.

Hydrothermal mineralization frequently involves fluid–rock interaction, which is essential for the transport and deposition of metal ions, especially in an intrusive-related mineralization system [4,199–201]. Many investigations have demonstrated that changes in the physicochemical properties of fluids as a result of fluid–rock interactions affect metal solubility and mineral precipitation [202–205]. Different hydrothermal alteration types are characteristics of porphyry molybdenum mineralization, and phyllic alteration is frequently seen as a sign of prospecting [201,203,205,206], as indicated by the fact that molybdenum mineralization in the deposit is spatially related to phyllic alteration, and plagioclase and K-feldspar of the ore-bearing granite porphyry tend to be replaced by quartz and sericite in

stage 1 (Figure 4b,e). Phyllic alteration lowered the H^+ contents of the hydrothermal fluids and enriched the reduced sulfur (S^{2-}), which mixed with Mo^{2+} to generate molybdenite. The following formulas reflect the pertinent reactions:



Therefore, we provide a preliminary argument that phyllic alteration could benefit the deposition of molybdenite at Lower Urgen. Nevertheless, a more detailed explanation to this conclusion is beyond the scope of our current study and additional alteration mineralogical and geochemical research is necessary before a full understanding can be attained.

Numerous studies have shown that fluid mixing is a crucial factor in the production of base metal sulfide deposits because it can dilute and cool hydrothermal solutions, which causes enormous sulfide mineral depositions [207–211]. Mineral deposition occurs when the solubility of metal ions in the fluids surpasses saturation, and substantial deposition occurs as the solubility is dramatically decreased [208]. In the Lower Urgen deposit, the continuous fluid immiscibility in stages 1 and 2 would have increased the permeability of the host granite porphyry stock, and further accelerated meteoric water circulation. Stage 2 fluids have much lower salinity and homogenization temperatures than stage 1 fluids (Figure 12). Additionally, stage 2 fluids have more depleted $\delta^{18}O_{\text{fluid}}$ values than stage 1 fluids (Figure 8). These features collectively demonstrate the existence of fluid mixing processes in stage 2. To summarize, fluid mixing propelled the polymetallic sulfide mineralization in stage 2 at Lower Urgen. The progressive incursion of meteoric water into the magmatic–hydrothermal system might cause considerable cooling, the instability of metal chloride complexes, and sulfide deposition.

In conclusion, stage 1 molybdenite deposition is primarily controlled through fluid immiscibility and fluid–rock interaction. The increasing injection of meteoric water into the hydrothermal system and fluid immiscibility collectively controlled the massive deposition of polymetallic sulfides in stage 2.

6.5. Metallogenic Model for the Lower Urgen Magmatic–Hydrothermal System

Especially for intrusion-related magmatic–hydrothermal deposits, the development of a metallogenic model may successfully direct the investigation of the ore deposit and increase the successful rate of prospecting and prediction [4,212]. We construct the metallogenic model for the Lower Urgen molybdenum deposit upon the above discussion and previous research, as outlined below.

Due to the closure of the MOO, the surveyed region experienced an extensional environment in the Late Jurassic and Early Cretaceous, which promoted the partial melting of the lower crust and produced ore-bearing granitic magmas [25,50,213–218]. As a lithophile element, molybdenum tends to be abundant in the crust but deficient in the mantle [219]. Consequently, a potential source for molybdenum mineralization might be the lower crust under the Lower Urgen region. Metallic elements are partitioned into the melt through partial melting of the protolith. The ore-bearing granite porphyry, which represents the parental rock and served as a constant source of hot, ore-rich fluids for the generation of the hydrothermal mineralization system, was emplaced at about 142.3 Ma. The potassic and phyllic alteration zones were generated by these fluids accumulating at the cupola of the mineralization intrusion and interacting with cooling granite porphyry (Figure 2c). In the meantime, intense and widespread fluid immiscibility was created through the constant ascent and decompression of mineralizing fluids. Stage 1 fluids belong to a NaCl–H₂O–

CO₂ system and contain bimodal salinities (5.0–11.9 and 30.1–50.8 wt% NaCl equiv.) and have medium–high temperatures (240–430 °C). Intense fluid immiscibility and fluid–rock interaction caused an increase in pH and a drop in temperature, which significantly reduced the solubility of molybdenum and aided in the precipitation of molybdenite. The molybdenum mineralization stage was characterized by widespread molybdenum-bearing quartz veinlets and disseminated molybdenite in the granite porphyry. In stage 2, massive meteoric water mixed with the evolved magmatic–hydrothermal fluids through localized regional hydraulic fractured and brecciated zones. Stage 2 fluids have salinities and homogenization temperatures of 3.0–9.1 wt% NaCl equiv. and 180–280 °C, respectively, and belong to a NaCl–H₂O–CO₂ system. The molybdenum mineralization came to an end with the extinction of veinlet-disseminated- and vein-type quartz–molybdenite(–pyrite) ores. The constant infiltration of meteoric water diluted ore-forming fluids and decreased their temperature. This process, combined with extensive fluid immiscibility, collectively led to the large-scale decoupling of base metal complexes and promoted the massive deposition of polymetallic sulfides. Stage 3 fluids belong to a NaCl–H₂O system and have salinities of 0.2 to 7.9 wt% NaCl equiv. and homogenization temperatures of 120 to 220 °C, suggesting a hydrothermal environment with low salinity and temperature. The hydrothermal fluids were governed by meteoric water as the pressure of the system was dropped. The fluids produced quartz and calcite as precipitates. The absence of ore minerals in the veins of this stage suggests that the fluids are no longer useful for mineralization, signaling the termination of the hydrothermal process in the Lower Urgen region.

7. Conclusions

(1) Molybdenite Re–Os dating yields two model ages of 141.2 ± 1.5 and 147.7 ± 1.7 Ma for the Lower Urgen molybdenum deposit. The new geochronological data indicate that the molybdenum mineralization event in the Lower Urgen area is consistent with the intensive and extensive Late Jurassic–Early Cretaceous molybdenum mineralization events in NE China.

(2) Three hydrothermal stages of the Lower Urgen molybdenum deposit can be distinguished: (i) quartz–molybdenite(–pyrite) stage—ore-forming fluids have medium–high temperatures (240–430 °C) and bimodal salinities (5.0–11.9 and 30.1–50.8 wt% NaCl equiv.) and belong to a NaCl–H₂O–CO₂ system; (ii) quartz–polymetallic sulfide stage—ore-forming fluids have medium temperatures (180–280 °C) and low salinities (3.0–9.1 wt% NaCl equiv.) and belong to a NaCl–H₂O–CO₂ system; and (iii) quartz–carbonate stage—fluids have low temperatures (120–220 °C) and low salinities (0.2–7.9 wt% NaCl equiv.) and belong to a NaCl–H₂O system.

(3) Hydrogen–oxygen isotope results indicate that the mineralizing fluids initially had a magmatic source with the progressive incursion of meteoric water. Sulfur–lead isotopic compositions indicate that the mineralizing materials have a genetic relationship with ore-bearing granite porphyry, and sulfur and lead are magmatically derived.

(4) Fluid immiscibility and fluid–rock interaction are the predominant mechanisms for molybdenite deposition in stage 1. Fluid mixing and immiscibility are cooperatively accountable for the massive deposition of polymetallic sulfides in stage 2.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/min13091189/s1>, Table S1: Microthermometry data for fluid inclusions in quartz from the Lower Urgen molybdenum deposit; Table S2: Molybdenite Re–Os isochron ages for Mesozoic molybdenum deposits in NE China [26,41,43,46,48,49,52–54,57,59,61,62,64,65,67,72,73,75,79,81,83–86,143,153–156,158–165,167–171].

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Data Availability Statement: The data presented in this study are available in the article and Supplementary Materials.

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