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N₂-rich fluid in the vein-type Yangjingou scheelite deposit, Yanbian, NE China

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Nearly pure N₂ fluid inclusions ($T_h(L) = -151 \sim -168^\circ\text{C}$; $T_h(V) = -150.3^\circ\text{C}$) were identified in W-mineralized quartz veins from the Yangjingou scheelite deposit, in the eastern Yanbian area, NE China. Other fluid inclusion populations include N₂-CO₂, NaCl-H₂O $\pm$ N₂ and CO₂ $\pm$ N₂-NaCl-H₂O, but no hydrocarbons were detected. The host rocks are part of the Wudaogou Group metamorphic series, which mainly consist of Ca-rich mica schist. Subhedral sulfide minerals occur in early disseminated W-mineralized quartz veins, or have partially replaced early scheelite. T_{hN_2} and $T_{hN_2-H_2O}$ indicate N₂ fluid-trapping from 315 °C to 410 °C and from 80 MPa to 350 MPa. Oxygen and hydrogen isotopic data ($\delta D = -74.9\text{‰} \sim -77\text{‰}$, $\delta^{18}\text{O} = 9.6\text{‰} \sim 12\text{‰}$, V-SMOW) suggest that the mineralizing fluids were composed of mixed magmatic and metamorphic water, N₂-rich inclusions ($\delta^{15}\text{N} = -0.5\text{‰}$ to 1.4‰) indicate fluid-rock interaction with metamorphic rocks. The N₂-rich fluid was closely associated with scheelite precipitation. During thermal decomposition under high oxygen fugacity conditions, which occurred synchronously with metamorphism and magmatic activity, large amounts of N₂ were liberated from NH₄⁺-micas, which then accumulated in the parent fluid of the quartz scheelite veins.

Nitrogen is the dominant constituent of the atmosphere and a key component in the biosphere. High-density CO₂-N₂ inclusions have been detected in high-grade metamorphic rocks from the upper mantle and lower crust (i.e., granulites and eclogites)^{1–3}. In silicates, under conditions of elevated temperatures, low water activity, and high oxygen fugacity, N₂ is favorably released from minerals containing ammonium (e.g., feldspar and mica)^{4,5}.

Scheelite containing nitrogen is most commonly recognized to be traced from sedimentary rocks⁶. In sedimentary-type deposits, tungsten (W) is liberated as a result of exhalative processes, forming stratiform scheelite⁶, in which mineralizing fluids containing CH₄ and N₂ are generally attributed to *in situ* organic matter⁶. Several examples of scheelite deposits related to metamorphic hydrothermal fluids are reported to contain small amounts of N₂^{7,8}. These types of scheelite deposits are of interest to the geologist, because they are related to Au deposits⁹. Furthermore, Gibert⁸ found that the addition of only 5% N₂ would decrease the solubility of scheelite in micaschists from 40 ppm to less than 3 ppm W, indicating that N₂ may drive scheelite participation.

Nearly pure N₂ (>88 mol%) was identified in fluid inclusions in W-mineralized quartz veins, which is absent of hydrocarbons. Previous studies have shown that NaCl-H₂O and CO₂ fluid inclusions are common in ore-forming fluids; however, the presence of N₂-rich fluids in ore deposits is rarely reported. This study aims to identify the origin of the W-mineralizing fluid and the formation of the N₂-rich fluid inclusions by combining petrography, Raman microspectroscopy, H, O and N isotope geochemistry, and microthermometry on fluid inclusions. Results from this study will improve our understanding of how N₂ modulate scheelite mineralization.

Geology of the Yangjingou scheelite deposit

The Yangjingou scheelite is the largest identified scheelite deposit in the Yanbian belt, NE China. It is located between the Cuihongshan and Sanjiazhi scheelite deposits in the Heilongjiang-Jilin metallogenic belt, 8 km south of the Xiaoxinancha Au deposit, approximately 25 km east of the Russian border (Fig. 1c). In this deposit, the main economic mineral is scheelite, accompanied by minor Au, Cu, Mo, Fe, and P mineralization. The area is dominated by low-grade metamorphic rocks of the Wudaogou Group, which formed during a regional episode of low-grade epidote to low-grade amphibolite metamorphism. Regional stratigraphic correlations, metamorphic studies, and U–Pb geochronology from metamorphic detrital zircons indicate that sedimentation and regional metamorphism dated 323 ± 23 Ma¹⁰ and 266–249 Ma, respectively¹¹. The Wudaogou Group is subdivided into

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Figure 1. Geological map showing the main units in the Jilin and Heilongjiang metallogenic belt as well as ore deposit locations in the Yanbian area. (A) Location of the Central Asian Orogenic Belt and NE China; (B) Location of the Jilin and Heilongjiang metallogenic belt; (C) Location of the major tectonic units in the Jilin and Heilongjiang metallogenic belt (After Wu⁵⁵; https://www.researchgate.net/publication/229317465_Geochronology_of_the_Phanerozoic_granitoids_in_Northeastern_China).

the lower Madida Formation, the middle Yangjingou Formation, and the upper Xiangfangzi Formation¹². The rocks from these formations are composed of muscovite, K-feldspar, amphibolite, plagioclase, quartz, and small amounts of cordierite, andalusite, rutile and kaolinite^{12,13}.

The Yangjingou scheelite deposit (Fig. 2) is located within a N-S-oriented asymmetrical syncline on the western limb of the Wudaogou synclinorium. The eastern limb dips 45–50°NE, and the western limb dips 55–60°NW (and locally up to 75–80°). The mine is situated in a NW-SE-oriented secondary syncline with an E-W-striking fold axis, crosscut by a N-S- to NW-SE-striking fault. The eastern limb of the synclinorium has been extensively modified by magmatic intrusions, whereas the western limb remains relatively unaltered. The scheelite ore bodies are structurally controlled by 3 secondary N-S-, NW-SE-, and NNW-SSE-striking normal faults. The N-S-striking fault is 2 km in length, dips 60–80°NW and lies parallel to the principle compressional fault in the region. The

Figure 2. Geological map of the Yangjingou scheelite deposit (After Ren^{14,18}, http://www.ysxb.ac.cn/ysxb/ch/reader/create_pdf.aspx?file_no=20101222&flag=1&journal_id=ysxb&year_id=2010).

0.8–1.0 km NW-NNW-oriented fault, which dips 40–70°SW and lies oblique to the major compressional fault and is extensively mineralized

Several generations of magmatic intrusions, including late Hercynian granodiorite (267 ± 1 Ma)¹⁴ and early Indosinian Yangjingou granodiorite (249.4 ± 2.7 Ma)¹⁵ have locally deformed rocks of the Wudaogou Group. Based on the Yangjingou granodiorite chemical signature, a transition from I- to S-type magmatism is observed, interpreted as a result of subduction¹⁶. Yanshanian intrusives, including monzonitic granodiorite (178.5–197 Ma)¹⁷ and dioritic porphyry dykes (120.73–157.27 Ma)¹⁷ were later emplaced within zones of pre-existing structural weakness. Previous studies have revealed a close association between Indosinian magmatism and W mineralization in the Yangjingou deposit^{16,18}. Furthermore, Shan¹⁹ and Hu¹⁷ suggest that the dikes present in our study area are genetically related to an unexposed granite intrusion.

The scheelite ore bodies are mainly hosted in Ca-rich mica schists. The deposit can be subdivided into a southern and a northern ore block, separated by a N-W-trending fault (Fig. 2). In the northern ore block (Fig. 3b),

Figure 3. (a) Cross section of the southern ore block in the Yangjingou scheelite deposit; (b) Cross section of the northern ore block in the Yangjingou scheelite deposit (After Shan¹⁹; http://kckc.org.cn/ch/reader/create_pdf.aspx?file_no=2010Z106&year_id=2010&quarter_id=Z1&falg=1).

mineralization is structurally controlled by normal faults striking 295–315° and dipping 65–75°. Mineralization occurs in quartz stringers and large quartz veins that have been emplaced along intraformational faults, which partially crosscut the upper Hercynian granodiorite. Individual veins are typically sub-parallel, appear as lenticular or spindle-shaped bodies, exhibit pinching and swelling, and measure approximately 10 cm in width. The ore bodies exhibit a total length of more than 900 m, a width from 60 to 425 m, and a stacking thickness of approximately 95 m.

Mineralization in the southern ore block is structurally controlled by normal faults striking 300–350° and dipping 60–75° (Fig. 3a). The width of individual veins ranges from 2 to 10 cm (locally reaching up to 65 cm). The total length of the ore bodies is approximately 800–1400 m, with a maximum width of 450 m. The scheelite-bearing veins in both the northern and southern ore blocks share similar characteristics in terms of their orientation and geometry.

The average W oxide (WO₃) grade of the mine is 0.22% to 1.5%, reaching up to 5.25%, with accessory Au (0.49–0.79 g/t), Cu, Mo, Fe, and P¹⁹. Scheelite mineralization predominantly occurred via micro-vein dissemination and thin vein mineralization (Fig. 4a,b). The ore minerals include scheelite, pyrrhotite, pyrite, arsenopyrite, and sphalerite, while the gangue assemblage is comprised of quartz, muscovite, hornblende, andalusite, epidote, and actinolite. Sulfide minerals typically exhibit euhedral to subhedral crystal habits with granular embayments and metasomatic relict textures. Scheelite grains are subhedral (Fig. 4f) and disseminated in microfractures within quartz veins with a low sulfide content (Fig. 4c). Arsenopyrite has replaced early scheelite minerals and occurs as euhedral-subhedral disseminations in W-mineralized quartz veins (Fig. 4c). Pyrite postdates pyrrhotite and together with chalcopyrite, replaces pyrrhotite. Based on the mineral assemblages, micro-textures and

Figure 4. (a and b) Scheelite paragenetic quartz veins (scheelite showing blue-fluorescence under the ultraviolet irradiation); (c) arsenopyrite replaced early scheelite minerals and existed in early disseminated W-mineralization quartz veins; (d) sphalerite and copper pyrites replacing pyrrhotite; (e) pyrrhotites replaced early scheelite; (f) subhedral scheelite; (g and h) actinolite, epidotization; (i) muscovite quartz schist.

associated alteration types, two stages of mineralization are distinguished: (1) the quartz-scheelite stage (oxide stage) and (2) the later pyrrhotite-arsenopyrite-pyrite stage (sulfide stage), with the quartz-scheelite stage being the major metallogenic stage. The alteration of the ore bodies mainly includes sericitization, actinolite, albization, carbonation, and epidotization (Fig. 4h,i,k).

Analysis and Methods

Fluid inclusions. Twenty-six highly transparent 100–300- μm doubly polished thick quartz plates of paragenetic scheelite quartz veins from the southern and northern ore blocks of the Yangjigou deposit were analysed. Fluid petrography and microthermometry analyses were performed at the Geological Fluid Analysis Center of Jilin University, Changchun, China. The microthermometric analysis of fluid inclusions was conducted with a Linkam THMSG 600 stage mounted on a Carl Zeiss Axiolab microscope (10×50) capable of temperature measurements from -196 to 600°C . The accuracy between 31°C and -100°C is better than $\pm 0.2^\circ\text{C}$ and better than 5°C at $>300^\circ\text{C}$. The heating/freezing rate is generally 0.2 – $1^\circ\text{C}/\text{min}$ but is reduced to $0.1^\circ\text{C}/\text{min}$ close to the phase transformation point. The FLUIDS^{20,21} software package used for the calculation of the isochors and the phase transition temperature of N_2 – CO_2 were plotted in the diagram of Thiery²² and Van den Kerkhof & Thiery²³ in order to determine vX properties of the fluid.

Raman microspectroscopy analysis. Raman analysis was performed at the Geological Fluid Analysis Center of Jilin University. The Raman instrument is a Renishaw RM-1000 and was mounted on an Olympus BX40 microscope. A 532 nm green diode-pumped solid state laser was used as an excitation source. The spectrum counting time was 30–60 s, the spectral resolution 1 – 2 cm^{-1} , and the laser beam diameter 1 – $2\text{ }\mu\text{m}$. A detailed description of the measurement procedure was provided by Wopenka²⁴. The measurements reveal that the major gaseous fluid inclusion components are N_2 and CO_2 . A large proportion of the inclusions show only a single strong band at 2328.2 – 2328.3 cm^{-1} , indicating pure N_2 , which is the first time pure N_2 inclusions have been observed in the W deposit (Fig. 5). Some of the inclusions feature peaks at 3399 – 3500 cm^{-1} , indicating the presence of water. The CO_2 component corresponds to the Fermi diad at 2328 – 2330 and 1280 – 1386 cm^{-1} .

Figure 5. Photomicrographs of representative fluid inclusion types at room temperature in the quartz–scheelite stage. Type I: pure N₂ fluid inclusions (a–c,g,u); Type II: CO₂–N₂ inclusions (o,m,n), occasionally solid CO₂ phase below –100 °C (n,r) and three phases under the –160 °C (o); Type IIIa: inclusions containing 10%–30% gas (e,f); Type IIIb, inclusions in which the proportion of the gaseous phase ranges from 70% to 95% (d,j,i), and the liquid phase of N₂ partially exists at temperatures below –150 °C (p). One phase (k) at room temperature and two phases below –160 °C (l); Type IV: NaCl–H₂O–CO₂ fluid inclusions (e). Representative Raman spectra of fluid inclusions related to the mineralizing fluid of the Yangjingou scheelite. Panel A shows that the vapour bubbles are mainly composed of N₂; panel B shows that the bubbles contain mainly N₂ and some CO₂; and panel C shows that the fluid inclusions are mainly composed of N₂ and H₂O.

Stable isotope analysis. The oxygen and hydrogen isotopic compositions of primary fluid inclusions in the main stage (oxide stage) of the disseminated scheelite quartz veins were analysed at the analytical laboratory of Beijing Research Institute of Uranium Geology (BRIUG), China, using a MAT253-type mass spectrometer. Grains (40–60 nm) were handpicked to ensure the absence of mineral impurities. Oxygen was liberated from quartz for isotopic analyses via quantitative reaction with BrF₅ using a CO₂ laser as a heat source. H₂O was first released by heating the samples to temperatures above 550 °C then reacted with zinc at 800 °C to produce hydrogen. The results are reported in per mil (‰) relative to the Vienna Standard Mean Ocean Water (VSMOW) standard, with precisions of ±2‰ for δD and ±0.2‰ for δ¹⁸O at the 1σ level. δ¹⁸O_{quartz} was measured in order to calculate the δ¹⁸O_{H₂O} values of hydrothermal fluids using the following equation:

$$1000 \ln \alpha_{\text{quartz-water}} = 3.38 \times 10^6 \cdot T^{-2} - 3.40,$$

where T represents the homogenization temperature of the fluid inclusions²⁵.

W-quartz vein	N ₂	N ₂ –CO ₂	CO ₂ ± N ₂ + H ₂ O + NaCl	H ₂ O + NaCl ± N ₂
YJ-1	N ₂ > 90 mole%	N ₂ : 46–76 mole%	Gas phase N ₂ : 8–24 mole%	Gas phase N ₂
		CO ₂ : 24–54 mole% v	CO ₂ : 76–92 mole%	a: Size 4–16 μm
	V _m : 35–60 cm ³ /mole	30–48 cm ³ /mole	Size: 6–20 μm	Fill 10%–20% Vol. Fracs
	Size: 8–10 μm	Size: 8–25 μm	Fill: CO ₂ /L _{H2O} 50–70% L _{CO2} /V _{CO2} : 70–85% 40–60	T _h 250°C–400°C
	Fill 100% Vol. Fracs	Fill 100% Vol. Fracs	T _h : 283–417°C	Sal 5.7–9.6 wt% NaCl eq
	T _h (L) _{N2} : –153°C~–168°C	T _{hN2} : –147.5°C~–163.2°C	T _{mCO2} : –62~–58.1°C	b: Fill 70–90% Vol. Fracs
	T _h (V) _{N2} : ~–150.3°C	T _{hCO2} : –46°C~–86°C	T _{CO2clathr} : 5.9–8.2°C	T _h 315–410°C
		T _{mCO2} : –60.9°C~–60.7°C	T _{hCO2} : 9.8°C~17.5°C	
YJ-3	N ₂ > 90 mole%	N ₂ : 42–78 mole% N ₂ : 46–76 mole%	Gas phase N ₂ : 8–24 mole%	Gas phase N ₂
		CO ₂ : 22–57 mole%	CO ₂ : 78–92 mole%	a: Size 4–14 μm
	V _m : 36–59 cm ³ /mole	V _m : 30–47 cm ³ /mole	Size: 8–18 μm	Fill: 10–15% Vol. Fracs
	Size: 4–28 μm	Size: 9–24 μm	Fill CO ₂ /L _{H2O} 55–75% L _{CO2} /V _{CO2} 70–85% 40–60	T _h : 271–381°C
	Fill 100% Vol. Fracs	Fill: 100% Vol. Fracs	T _h : 290–423°C	Sal 5.7–9.47 wt% NaCl eq
	T _{hN2} : –153.4°C~–168°C	T _{hN2} : –147.7°C~–162.3°C	T _{mCO2} : –62.1~–59.5°C	
	T _h (V) _{N2} : ~–150.4°C	T _{hCO2} : –46°C~–86°C	T _{CO2clathr} : 5.6–7.5°C	b: Fill 75–95%
		T _{mCO2} : –60.8°C~–60.7°C	T _{hCO2} : 10.6°C–18.4°C	T _h : 335–396°C
YJ-4	N ₂ > 88 mole%	N ₂ : 46–79 mole% N ₂ : 46–76 mole%	Gas phase N ₂ : 8–24 mole%	Gas phase N ₂
		CO ₂ : 21–54 mole%	CO ₂ : 78–89 mole%	a: Size 6–12 μm
	V _m : 34–59 cm ³ /mole	V _m : 31–45 cm ³ /mole	Size: 6–20 μm	Fill: 10–30% Vol. Fracs
	Size: 8–26 μm	Size: 8–26 μm	Fill CO ₂ /L _{H2O} 50–60% L _{CO2} /V _{CO2} : 70–90% 40–60	T _h : 285–378°C
	Fill 100% Vol. Fracs	Fill 100% Vol. Fracs	T _h : 290°C–422°C	Sal: 5.85–9.21 wt% NaCl eq
	T _{hN2} : –151.2°C~–167.5°C	T _{hN2} : –148.4°C~–162°C	T _{mCO2} : –65°C~–60.8°C	b: Fill 70–95% Vol. Fracs
	T _h (V) _{N2} : ~–150.3°C	T _{hCO2} : –46°C~–86°C	T _{CO2clathr} : 5.3°C–7.5°C	T _h : 339–410°C
		T _{mCO2} : –60.8°C~–60.7°C	T _{hCO2} : 10.8°C–20.5°C	
Transition		V _m : 30–62 cm ³ /mole	Sal: 4.87%–8.45 wt% NaCl eq	
	L+G->L(G)	H-type: S+L+V->S+L(G)->S+L+G->L+G->L(G) S-type: S+L+G->S+L(G)->L(G)	S->S+L->S+L+G->L+G->L	S->S+L->S+L+G->L+G->L(G)

Table 1. Overview of the four fluid inclusion types observed in mineralizing quartz veins in the Yangjiingou scheelite deposit.

Seven quartz samples from scheelite quartz veins were selected for N isotopic analysis. In order to exclude atmospheric interference, samples were degassed for 15 minutes under vacuum ($<10^{-3}$ Pa). N₂ was then directly released from fluid inclusions by heating the quartz samples in a high-purity quartz cell to temperatures above 600°C. The released N₂ was then separated using a chromatographic column cold trap²⁶. Nitrogen isotopic compositions of the samples are reported using δ notation, where $\delta^{15}\text{N}_{\text{sample}} (\text{‰}) = [({}^{15}\text{N}/{}^{14}\text{N})_{\text{sample}} / ({}^{15}\text{N}/{}^{14}\text{N})_{\text{standard}} - 1] \times 1000$. The results are reported in per mil (‰) relative to atmospheric N₂²⁷, and the precision is $\pm 1\text{‰}$ at the 1 σ level.

Results

Fluid inclusions. The criteria by Roedder²⁸ for defining primary, secondary and pseudosecondary inclusions were applied. However, microthermology measurements were conducted on primary fluid inclusions, because only primary inclusions represent W-mineralized fluid. Primary inclusions occur in isolation or as random clusters within intragranular quartz crystals²⁸. Our study focuses on the main W-mineralizing stage, i.e., the scheelite-quartz stage. Based on composition, phase proportion at room temperature (21°C) and phase transition during total homogenization, four types of fluid inclusions have been identified in quartz crystals from the scheelite paragenetic quartz veins: pure N₂ fluid inclusions (Type I), CO₂-N₂ fluid inclusions (Type II), CO₂ ± N₂-NCl-H₂O inclusions (Type III) and aqueous two-phase VL inclusions (Type IV; Table 1).

The Type I (pure N₂) fluid inclusions (Fig. 5a,b,c,g,u) occur as a single phase at room temperature and are 6–30 μm in size. The inclusions are mostly oval in shape or exhibit a negative crystal shape and are randomly distributed in quartz grains. Type I inclusions are identified as N₂ homogenizes to liquid or gas (L + V->L(G)) and are closely related to scheelite deposits, but have been rarely reported. At low temperatures, bubbles nucleate at –162°C~–182°C. The final homogenization of the liquid phase T_h(L) occurs between –151°C~–168°C,

Figure 6. (a) The homogenization temperature of the fluid inclusions (Type I, II, III and IV). (b) Salinity of type IIIa and IV fluid inclusions. (c) The P-T conditions of the fluid inclusions in the scheelite quartz veins in the Yangjingou scheelite deposit (molar volumes between 30 and 500 cm^3/mole) (After Kerkhof and Thiéry²³ and Winter⁵²). Numbers denote molar volumes in cm^3/mole ; numbers in brackets are the homogenization temperature of N_2 .

although a few Type I fluid inclusions homogenize to the gas phase at -150.3°C (Fig. 6a,c). Raman analysis of the Type I inclusions yields compositions of $>88\text{ mol}\%$ N_2 , with minor amounts of CO_2 exhibiting molar volumes of $42\text{--}150\text{ cm}^3/\text{mol}$ ^{22,23} (Fig. 6c). No other gases were identified.

The Type II ($\text{CO}_2\text{-N}_2$) inclusions (Fig. 5m,s) are $5\text{--}25\text{ }\mu\text{m}$ in size, and most are between $8\text{--}15\text{ }\mu\text{m}$. These inclusions exhibit euhedral and negative crystal habits and are randomly distributed in the quartz grains. During cooling, the inclusions show bubble and solid CO_2 nucleation. The phase transitions on warming follow one of two sequences: $\text{S}+\text{L}+\text{G} \rightarrow \text{S}+\text{L}(\text{G}) \rightarrow \text{S}+\text{L}+\text{G} \rightarrow \text{L}+\text{G} \rightarrow \text{L}(\text{G})$ (H-type, i.e. $T_h > T_m$), showing homogenization as the final phase transition or $\text{S}+\text{L}+\text{G} \rightarrow \text{S}+\text{L}(\text{G}) \rightarrow \text{L}(\text{G})$ (S-type, i.e. $T_h < T_m$) showing sublimation as the final phase transition^{29,30}. Bubbles of nitrogen nucleate between -178 and -159°C (Fig. 5o); solid CO_2 is infrequently observed below -100°C (Fig. 5n,r). In S-type inclusions the partial homogenization (T_{hN_2}) to a liquid (gas) of is between -163.2 and -147.5°C . Critical homogenization can be observed around -147°C and the total homogenization (T_{hCO_2}) is characterized by sublimation to liquid (gas) phase from $-86\text{--}69^\circ\text{C}$. The T_{hN_2} of H-type inclusions to the liquid (gas) phase coincided with critical homogenization and occurred between -149 and -148°C . The total homogenization (T_{hCO_2}) to liquid (gas) varied from -60.8 to -45.6°C with the T_{mCO_2} between -60.9 and -60.7°C . Raman spectroscopy shows that the inclusions are composed of $42\text{--}79\text{ mol}\%$ N_2 , and $21\text{--}58\text{ mol}\%$ CO_2 with molar volumes between 30 and $65\text{ cm}^3/\text{mole}$, in agreement with microthermometry results (Figs 6a and 7).

The Type III ($\text{NaCl-H}_2\text{O}$) inclusions contain liquid and gas at room temperature and have been subdivided into Type IIIa and Type IIIb populations. Type IIIa inclusions contain gas volume fractions of $<50\%$, where most are between 10 and 30% (Fig. 5f). N_2 less than 10% were infrequently detected in these inclusions. Fluid inclusions are generally $4\text{--}16\text{ }\mu\text{m}$ in size, clustering between approximately 6 and $10\text{ }\mu\text{m}$ and appear as elongated and spindle shapes, which are randomly distributed in quartz grain. These inclusions yield T_{mice} of -6.7°C to -3.5°C and homogenize to liquid between 250 and 400°C , predominantly between 300 and 375°C (Fig. 6a). Therefore, the salinity of these inclusions is 6–10 equiv. wt% NaCl²⁰ (Fig. 6b). In Type IIIb inclusions, the gas volume fractions are $>50\%$, where most are between 70–95% (Fig. 5d,j,i). The total homogenization temperature to the gas phase occurs between 314 and 409°C , predominantly between 334 and 381°C (Fig. 6a). The liquid phase of N_2 can be locally observed at temperatures below -150°C (Fig. 5p).

The Type IV ($\text{NaCl-H}_2\text{O-CO}_2 \pm \text{N}_2$) inclusions contain CO_2 gas, CO_2 liquid, and a saline solution at room temperature (Fig. 5e). The volume fraction of CO_2 bubbles in the inclusions exceed 40%, with the majority of the inclusions featuring volume fractions of 50–80%. The gas phase comprises 75–90% of this volume fraction. These primary inclusions show euhedral and irregular polygonal shapes. They occur in randomly distributed clusters in quartz grains and individual inclusions are small, measuring $4\text{--}20\text{ }\mu\text{m}$. Solid CO_2 melts at $-60.8\text{--}58.1^\circ\text{C}$, indicate the presence of minor N_2 . CO_2 clathrate melting occurs at $5.3\text{--}8.1^\circ\text{C}$ and the salinity of the inclusions ranges from 4 to 9 equiv. wt% NaCl (Fig. 6b). Partial homogenization of CO_2 to liquid occurs at $9.8\text{--}20.5^\circ\text{C}$, and total homogenization to liquid occurs at $283\text{--}423^\circ\text{C}$, predominantly at $320\text{--}402^\circ\text{C}$ (Fig. 6a).

Stable isotopes. The δD and $\delta^{18}\text{O}$ values of the W-mineralized quartz veins exhibit relatively narrow ranges ($-74.9\text{--}77\text{‰}$ and $9.6\text{--}12\text{‰}$, respectively; Table 2). Wood and Samson³¹ demonstrated that scheelite precipitation in W deposits hosted by siliceous rocks occurs at temperatures of $200\text{--}500^\circ\text{C}$. Consequently, the mode

Figure 7. vX diagrams calculated for the $\text{CO}_2\text{-N}_2$ system of the Yangjingou deposit showing low molar volumes ($v < 100 \text{ cm}^3/\text{mole}$). The thick red line G (SL) defines the difference between S - and H -type II inclusions. Inclusions plotting below the $L = G$ homogenize to gas, above the critical curve to liquid. Thin red solid line = homogenization ($T_{h\text{CO}_2}$). Dashed dotted red line = partial homogenization ($T_{h\text{N}_2}$). Thin black line = initial melting of CO_2 ($T_{m\text{CO}_2}$) (After Kerkhof and Thiéry²³; Thiéry *et al.*²²).

Mineral	Mineral	Sample	δD (‰)	$\delta^{18}\text{O}$ (‰)	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (‰)	$\delta^{15}\text{N}$ (‰)	
		Q11	-75	13.5	8.20		Zhang <i>et al.</i> ¹⁵
Yangjingou Scheelite deposit	W-mineralizing quartz vein	Y-1	-77	9.6	4.30	0.7	This study
		Y-2	-74.9	10.8	5.50	0.4	
		Y-3	-76.1	12	6.70	-0.2	
		Y-4	-76.7	10.6	5.30	-0.5	
		YJ-10				0.6	
		YJ-7				1.4	
		YJ-8				0.8	
Naozhi Au deposit	Au-mineralizing quartz veins	NB124-1	-123.8	4.598	-1.40		Huang <i>et al.</i> ⁴¹
		NB123	-97.3	7.525	0.53		
		NB601	-113.05	10.562	4.53		
		NB119	-90.62	4.583	-5.01		
Baishilazi W-deposit	W-mineralizing quartz veins	BS-4	-100.6	13.1	3.14		Zhao ¹⁶
		BS3-1	-102.4	12.6	2.64		
		BS-2	-100.4	12.4	2.44		
		BS-6	-90.8	12.4	2.44		
Nyakabingo W-deposit	W-mineralizing quartz veins	Ny09FD02	-57		15.4		S. Dewaele ⁷
		Ny09FD08	-64		15.6		
		Ny09FD11	-61		14.9		

Table 2. Hydrogen and oxygen isotopic compositions of the main stage quartz in the Yangjingou scheelite deposit.

homogenization temperature of 375°C in the Type IIb fluid inclusions was chosen to calculate the $\delta^{18}\text{O}$ value of the water in the ore-forming fluid. In the $\delta^{18}\text{O}$ - δD diagram, the calculated $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values (4.96 – 7.36 ‰; Fig. 8a) fall within or close to the fields of metamorphic water and primary magmatic water. The $\delta^{15}\text{N}$ values of the N_2 extracted from the fluid inclusions vary from -0.5 ‰ to 1.4 ‰ (Table 2; Fig. 8b). In the $\delta^{15}\text{N}$ graph, all the samples from the W-mineralized quartz veins fall in the range characterized by sub-greenschist-facies metamorphism.

Discussion

Nitrogen in ore-forming fluids. The presence of N in W-bearing mineralizing fluids has previously been reported^{7,8,32}; however, fluids with $>50 \text{ mol}\%$ N_2 are rare. Lin³³ assumed that the N_2 -rich fluid inclusions identified at the Dongchuan Cu deposit resulted from either mantle devolatilization during the break-up of Rodinia or the trapping of gas derived from decomposing organic materials. In contrast, the Yangjingou deposit formed in a compressional environment during the closure of the Paleo-Asian Ocean. There is no evidence for mantle degassing during regional orogenic activity in this area. Therefore, the presence of N_2 in the deposit may be associated with plate collision, ocean closure, regional Barrovian metamorphism, and eclogite-facies metapelites^{34,35}.

Figure 8. (a) Plot of δD values versus $\delta^{18}O$ values for the ore-forming fluids related to the Yangjingou scheelite deposit (modified after Taylor⁵⁶). The data are from the following sources: Naozhi Au deposit (Huang *et al.*⁴¹), Xiaoxinancha Au deposit (Wang⁴²), Baishilazi W deposit (Zhao¹⁶) in Yanbian area and Nyakabingo W deposit, central Africa (Dewaele *et al.*⁷). (b) Nitrogen isotopic compositions of the fluid inclusions in the Yangjingou scheelite deposit and (After Bebout *et al.*²⁷).

Under alkaline conditions, W is transported in the form of H_2WO_4 , M_2WO_4 ($M = Na, K$), and WO_4^{2-} complexes in W-mineralizing fluid. The presence of NH_4^+ in the solution stabilizes the W polyacid, thereby increasing its compatibility in migrating fluids³⁶. The stability of NH_4^+ (substituting for K^+) widely depends on the metamorphic and oxygen fugacity conditions^{27,37}. Nevertheless, under metamorphic conditions, NH_4^+ -bearing minerals may release N_2 (350–600 °C) or NH_3 (650–700 °C) at higher oxygen fugacity and concentrate in inclusions. The following equation illustrates the production of N_2 under oxidizing conditions³⁸:

The main cause for scheelite precipitation is an increase in the activity of Ca^{2+} , which results in the chemical equilibration of the mineralizing fluid with the host rock and has been recorded at a range of pressures and temperatures³². The addition of the non-polar volatile N_2 via water-rock interactions in mica may decrease scheelite solubility in common metamorphic assemblages. N_2 has been demonstrated to dominate changes in the distribution of W aqueous species and increase coefficient activity⁸. In other words, an increase in the N_2 content in the mineralizing fluid may promote scheelite precipitation.

N_2 -rich fluids in the Yangjingou scheelite deposit. *Nature of the ore-forming fluids.* The ore must have precipitated from H_2O - CO_2 - N_2 - $NaCl$ -bearing fluids with low to moderate salinity at moderate to high temperatures. The only volatile components in this fluid are CO_2 and N_2 ; hydrocarbons (i.e., CH_4) have not been detected. From the vx plot (Figs 6, 7c) we can observe that the fluid inclusions richer in CO_2 (30–65 cm³/mol) have lower molar volumes than those richer in N_2 (42–150 cm³/mol). This has been observed in many metamorphic areas^{3,29} indicating that CO_2 and N_2 may not have the same origin³⁸. The homogenization temperatures of N_2 (T_{hN_2}) and $H_2O \pm N_2$ - $NaCl$ (T_{hH_2O}) constrain the pressure-temperature (P-T) conditions of trapping to 315–410 °C at 80–350 MPa (Fig. 6c), suggesting that the W mineralization occurred during late stage greenschist-facies metamorphism at temperature of ~300–600 °C³⁹.

Stable isotopes. The stable isotopic composition of a vein provides direct information regarding the transport processes during vein formation²⁵. Several sources have been suggested for mineralizing fluids in hydrothermal

systems. These include magmatic origin, in which fluids evolve in relatively closed systems. Such mineralizing fluids are only observed in association with vein-type wolframite deposits⁴⁰. Several models that result in mineral precipitation from magmatic fluids of mixed origin are as follows (Fig. 8a): 1) a dominantly magmatic fluid mixing with meteoric waters (e.g., the Xiaoxinancha porphyry Cu–Au deposit, Naozhi alteration Au deposit and Bashilazi skarn-type scheelite deposits)^{16,41,42} and 2) the interaction of magmatic fluids with NH_4^+ -rich host rocks, and/or mixing with metamorphic fluids in equilibrium with metasedimentary lithologies (e.g., the vein-type Nyakabingo W deposit)⁷.

Low $\delta^{18}\text{O}$ and δD of the Yangjingou scheelite deposit indicate that the magmatic component of the fluid played a more dominant role in this deposit compared to the Nyakabingo deposit, in which the mineralizing fluid was metamorphic (Fig. 8a). Earlier C and S isotopic studies yielded $\delta^{13}\text{C}_{\text{V-PDB}}$ values of -3.4‰ to -6.5‰ for CO_2 and $\delta^{34}\text{S}_{\text{V-CDT}}$ values of -0.4‰ to 4.7‰ for pyrrhotite, pyrite, and arsenopyrite in scheelite-mineralized veins¹⁵, consistent with mantle values ($\delta^{13}\text{C}_{\text{V-PDB}} = -5\text{‰}$ and $\delta^{34}\text{S}_{\text{V-CDT}} = \pm 5\text{‰}$), demonstrating that the fluid was derived from the mantle. However, compared with magmatic hydrothermal deposits in this area (Fig. 8a), the Yangjingou scheelite deposit shows different δD values which may be interpreted in one of two ways: 1) the original mineralizing magmatic hydrothermal fluid interacted with NH_4^+ -rich metamorphic minerals and/or mixed with metamorphic fluids during host rock equilibration or 2) the mineralizing fluid of magmatic origin, mixed with low- δD meteoric waters. Because W-mineralized in the presence of Ca-mica schist host rock coupled with N_2 -rich fluid inclusions in the Yangjingou deposit, the first explanation is preferred.

The N isotopic system may potentially provide a detailed record of fluid–rock interaction characteristics and other mixing processes in the crust and mantle³⁷. N_2 has been shown to be released during metamorphism and the breakdown of NH_4^+ -bearing minerals, such as biotite, cordierite, and white mica⁴³. During metamorphism, isotopically “light” N is preferentially fractionated into metamorphic fluids^{39,44–46}, and the $\delta^{15}\text{N}$ values of fluid inclusions in quartz veins in low-grade metamorphic rocks yield values ranging from -3 to 5‰ ³¹. Similarly, the W-mineralized quartz veins in the Yangjingou deposit feature low $\delta^{15}\text{N}$ values (Fig. 8b), which may be attributed to fluid–rock interaction and the continuous liberation of N_2 in a metamorphic environment. The “light” N is preferentially fractionated into the fluid and is then trapped in the fluid inclusions.

The origin of the Yangjingou N_2 -rich fluid. The Wudaogou Group host rock was deposited at $323 \pm 23 \text{ Ma}$ ¹⁰. From 269–228 Ma, the tectonic regime of the region was dominated by the subduction of the Paleo-Asian oceanic plate beneath the North China plate⁴⁷. Regional greenschist- to epidote-amphibolite-facies metamorphism occurred between $269 \pm 4 \text{ Ma}$ and $249 \pm 4 \text{ Ma}$ ¹³. The age of muscovite crystallization in the W-mineralized quartz veins is $230.79 \pm 1.19 \text{ Ma}$ ¹⁶, indicating that W mineralization occurred in the earliest Late Triassic and during late-stage Wudaogou Group metamorphism. Therefore, the fluid system containing $\text{N}_2 \pm \text{CO}_2\text{--H}_2\text{O--NaCl}$ was intimately associated with complex multiphase tectonics and magmatic activity.

There are three mechanisms by which $\text{N}_2 \pm \text{CO}_2$ may have entered the mineralizing system: 1) trapping of a volatile phase separated from its parent $\text{H}_2\text{O--NaCl--CO}_2\text{--N}_2$ -rich fluid, 2) mixing of a magmatic–hydrothermal $\text{CO}_2\text{--H}_2\text{O}$ -rich fluid with N_2 released via the thermal decomposition of NH_4^+ -bearing minerals, or 3) $\text{CO}_2\text{--N}_2$ degassing of the mantle.

The stable isotope data in this study indicate that the mineralizing fluid was of a mixed magmatic and metamorphic origin. Magmatic melt inclusion studies have shown that CO_2 is released during magmatic differentiation^{48,49}, producing a distinct $\delta^{13}\text{C}$ signature¹⁷. Meanwhile, the Wudaogou Group contributed Ca^{2+} to the system, facilitating the precipitation of $\text{Ca}(\text{WO})_4$. Within this metamorphic environment, N occurs as NH_4^+ , which substitutes for K^+ in detrital phases such as K-feldspar, authigenic clays and illite. With increasing pressure and temperature, both feldspar and clays participate in low-grade metamorphic reactions, and illite gradually transforms into micas⁵⁰. During this transformation, a large amount of carbon is released in the form of CO_2 due to decarbonization during progressive metamorphism. Moreover, the reported content of CO_2 in schist ($<0.25\%$) is notably lower than that in clay and shale ($2.5\text{--}5\%$)³⁶. Thus, the contribution of organic matter to the mineralizing fluid was negligible. No CH_4 was identified in the W-mineralizing fluid, which may be due to the high oxygen fugacity⁵¹. Subsequently, Ca^{2+} from the Ca-rich mica schist country rocks was incorporated into the mineralizing fluid. The P–T conditions of the Yangjingou deposit ($315\text{--}410^\circ\text{C}$ at $110\text{--}350 \text{ MPa}$) are lower than greenschist-facies P–T conditions ($350\text{--}550^\circ\text{C}$ at $150\text{--}1100 \text{ MPa}$)⁵², indicating that scheelite mineralization likely occurred in the later stages of Wudaogou Group metamorphism. Additionally, the $\delta^{15}\text{N}$ values of the W-mineralized quartz veins show that water–rock interaction occurred under sub-greenschist-facies conditions. However, minor mantle N_2 participation cannot be completely ruled out.

Yangjingou scheelite mineralization is related to the intrusion of granodiorites at $249 \pm 2.7 \text{ Ma}$ ¹⁶, synchronous with Wudaogou Group metamorphism. A/CNK ($1.1\text{--}1.18$) and $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ($2.45\text{--}7.06$)¹⁶ major element values are characteristic of alkali series I- to S-type transient magmatism. The volatile component of the melts was influenced by pressure, which affected the volatile solubility in the magma during ascent. With decreasing pressure, gas was liberated from the magma⁵³, resulting in an increasing volume of CO_2 . CO_2 dissolves relatively readily in intermediate-alkaline magmas, leading to more widespread and more rapid emplacement of mineralizing fluids⁴⁶. Under these conditions, the diffusion of the W-rich mineralizing fluid was accelerated along interformational structures, causing the fluid to migrate to and rapidly expand into the host rocks of the Wudaogou Group. Only minor N_2 ($<0.25 \text{ mol}\%$)⁵⁴ was identified in fluid inclusions in the Xiaoxinancha Cu–Au porphyry deposit ($123.35 \pm 0.8 \text{ Ma}$)⁴², which is younger than the deposits in the Wudaogou Group and other stratigraphic units. The high concentration of N_2 observed in the scheelite deposits cannot simply be attributed to organic-rich sedimentary rocks. Findings from this study demonstrate that N_2 -rich fluids are closely related to the degree of metamorphism and magmatic activity.

Thus, we assume that the $\text{N}_2 \pm \text{CO}_2$ fluid was a product of late-stage Wudaogou Group metamorphism, which caused $\text{H}_2\text{O--NaCl--CO}_2$ -bearing magmatic–hydrothermal fluids containing HWO_4^- and MWO_4^- to migrate

Figure 9. The model of the mineralization of the Yangjingou scheelite deposit under the influence of both magmatism and metamorphism. Magmatic–hydrothermal CO_2 – H_2O -rich fluid interacted with the host rock and mixed with N_2 -rich fluids during migration, which caused scheelite participation.

through fractures and pre-existing structural weaknesses via fluid circulation, thereby promoting interaction with metamorphic wall rocks (Fig. 9). An initial increase in P–T conditions at ~269 Ma resulted in early low grade metamorphic reactions that transformed feldspar and clays within illite into micas. During this process, NH_4^+ substituted for K^+ , resulting in an increase in NH_4^+ within the constituent minerals of the Ca-rich mica schists⁵⁰. During late-stage metamorphism (~249 Ma), particularly under greenschist-facies conditions, NH_4^+ was released via continuous metamorphism or thermal decomposition (i.e., complete breakdown of host minerals, such as mica)^{27,50}. Simultaneously (~249 Ma), the circulation of a magmatic–hydrothermal W-mineralizing fluid under high oxygen fugacity conditions transferred heat (~400 °C) to the surrounding metamorphic rock and broke down micas in the host rock^{37,51}. Within an oxidizing environment at this temperature range, large amounts of N_2 were released from the NH_4^+ -bearing host rocks and stabilized into fluid⁴³. The addition of sufficient amounts of N_2 to the mineralizing fluid increased activity coefficients and catalysed the saturation of Ca^{2+} and WO_4^{2-} , greatly decreasing the scheelite solubility and accelerating scheelite precipitation. Moreover, saturated fluids, driven by advection, ascended into the surrounding country rock, resulting in alteration (albitization, chloritization, epidotization, and sericitization) and the incorporation of H_2O into new minerals, leaving $\text{N}_2 \pm \text{CO}_2$ trapped in quartz inclusions. Thus, the N_2 -rich fluid represents W-mineralizing fluid evolution and is indicative of W fluid saturation and scheelite precipitation.

Conclusions

1. Nearly pure N_2 (>88 mol%) fluid inclusions have been identified in W-bearing quartz veins in the Yangjingou deposit.
2. Four fluid inclusion populations have been identified in the deposit:
 - Type I: N_2 -rich inclusions (N_2 >88 mol%, $T_h(\text{L})_{\text{N}_2} = -151$ to -168 °C, $T_h(\text{V})_{\text{N}_2} = -150.3$ °C, 42 – 150 cm³/mole).
 - Type II: $\text{N}_2 \pm \text{CO}_2$ inclusions ($\text{N}_2 = 42$ – 79 mol%, $T_{h\text{N}_2} = -150$ to -163 °C, $T_{h\text{CO}_2} = -45.6$ to -86.1 °C, $\text{CO}_2 = 21$ – 58 mol%, 30 – 65 cm³/mole).
 - Type III: NaCl– H_2O inclusions (a: $T_h = 250$ – 400 °C, 6–10 equiv. wt% NaCl; b: $T_h = 315$ – 410 °C).
 - Type IV: $\text{CO}_2 \pm \text{N}_2$ –NaCl– H_2O inclusions ($\text{CO}_2 = 76$ – 92 mol%, $T_h = 283$ – 423 °C, 4–9 equiv. wt% NaCl).
3. The fluid inclusions were trapped at 315–410 °C and 80–350 MPa. The NaCl– H_2O – CO_2 fluids were magmatic–hydrothermal in origin, and the N_2 was derived from the breakdown of NH_4^+ -bearing minerals during alteration.
4. Hydrogen and oxygen isotopic data indicate that the mineralizing fluids were of a mixed magmatic and metamorphic origin, and the nitrogen isotopic data from the W-mineralized quartz veins suggest that water–rock interaction occurred under low greenschist-facies conditions.
5. The N_2 -rich fluid was intimately associated with the scheelite precipitation. During alteration under high oxygen fugacity conditions, N_2 was released from NH_4^+ -bearing minerals. The N_2 -rich fluid represents the W-mineralizing fluid evolution, following W saturation and scheelite precipitation. Therefore, areas that have experienced regional metamorphism (orogenesis) and exhibit similar geologic histories to the Yanbian area in NE China are likely candidates for scheelite precipitation as observed in the Yangjingou deposit. In this study, we demonstrate that scheelite precipitation can be genetically related to almost pure N_2 fluid inclusions. The presence of the almost pure N_2 fluid inclusions in these types of localities therefore can be used as a proxy for scheelite precipitation and thus, the presence of W $\pm$ Au deposits.

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Author Contributions

First author: Yicun Wang contributed to the analysis of fluid inclusions, paper writing and figure drawing. Corresponding author: Keyong Wang contributed to the sample collection and provided advice during the analysis and paper writing. Third author: Yassa Konare contributed to language polishing. All authors reviewed and approved the final manuscript.

Additional Information

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