In situ observations of tungsten speciation and partitioning behavior during fluid exsolution from granitic melt

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1. Introduction

Tungsten (W) deposits of economic importance are primarily of magmatic-hydrothermal origin, which are chemically and spatio-temporally related to granitic rocks, and are classified as wolframite (scheelite)-quartz vein (greisen), scheelite skarn, and porphyry types [1–3]. The average W content of the continental crust is ~1 ppm (1 ppm=1 μg/g) [4]. To form an economic W deposit (ore grade >1000 ppm) [5], W must be enriched at least ~1000 times. A series of geological processes have been proposed to account for such super-enrichment of W, including the formation of enriched source, partial melting, crystallization fractionation, fluid exsolution, and hydrothermal mineralization [1,6–8]. Apparently, fluid exsolution is an essential stage linking fractional crystallization of granitic magma and hydrothermal mineralization. Knowledge of the speciation and partitioning of W between fluid and melt during the fluid exsolution is vital toward establishing a sound W-mineralizing mechanism. However, this issue has not been well addressed before.

The partition coefficients of W between hydrothermal fluid and melt (D fluid/melt) reported previously show four orders of magnitude variation ranging from <0.01 to >10 (Table S1 online), hindering the quantitative description of the fluid exsolution and ore-forming processes. D fluid/melt was mainly obtained through analyses of the coexisting fluid and melt inclusions [9,10], and high temperature (T) and high pressure (P) experiments [1,11,12]. The former approach could be influenced by the acquisition of typical samples. For example, chemical equilibrium might not be achieved during crystallization, or the equilibrium was accomplished but not maintained during the formation of the melt and fluid inclusions [13,14]. If the W-bearing sample was sealed in noble metal
capsules (e.g., Pt, Au) during high $T$–$P$ experiments, significant loss of W into the capsule is predictable due to the alloy effect \cite{11, 15}. Continuous loss of W can seriously affect the partitioning equilibria, decreasing the validity and accuracy of the obtained $D_{\text{fluid/melt}}$ values \cite{15}. It should be noted that fluid unmixing and loss of elements from silicate glass during quenching will further complicate the experimental results \cite{16}.

Previous high $T$–$P$ experiments indicate that W occurs as tetrahedrally coordinated W(VI) (e.g., WO$_4^{2-}$) in silicate melt \cite{12, 17, 18}, and WO$_4^{2-}$, HWO$_4$, H$_2$WO$_4$, alkali-tungstates, and polymeric tungstates in hydrothermal fluids \cite{2, 12, 19, 20}. Obviously, the partitioning behavior of different W species cannot be determined through conventional ex situ (i.e., quenching) experiments. Alternatively, in situ spectroscopic analyses have been applied to decipher the species and distribution of some elements. For example, Borchert et al. \cite{21, 22} and Louvel et al. \cite{23} analyzed the fluid and coexisting melt phases in a hydrothermal diamond-anvil cell (HDAC) at $T < 950$ °C and $P < 2.2$ GPa using X-ray fluorescence or X-ray absorption spectroscopy, demonstrating that the partition coefficients of Br, Rb, Sr, Ba, La, Yb, and Y could be determined with high reliability. Colin et al. \cite{24} determined the partition coefficients of different sulfur species between aqueous fluid and silicate melts at 700 °C and 0.3–1.5 GPa using Raman spectroscopy and HDAC techniques. These studies show that such in situ high $T$–$P$ experiments can also be applied to study the species and partitioning of W during fluid exsolution.

In this study, the major goal is to reveal the geochemical behavior of W by Raman spectroscopic probing of the peralkaline (the aluminum saturation index (ASI) = 0.73, ASI = Al$_2$O$_3$/[Na$_2$O + K$_2$O + CaO]; Table S2 online) and peraluminous (ASI = 1.17; Table S2 online) melts, and the coexisting aqueous fluid at elevated $T$–$P$ conditions (up to 800 °C and 1.08 GPa). To accomplish this, the specific objectives of this work are: (1) collect in situ Raman spectra of W-bearing melt and fluid phases at high $T$ and high $P$; (2) document the species of silicate, H$_2$O, and W in melt and fluid phases; (3) determine the $D_{\text{fluid/melt}}$ of individual and total W species, and investigate the effects of $T$ and $P$ on the partitioning behavior; and (4) simulate the fluid exsolution process based on Rayleigh fractionation model and the obtained $D_{\text{fluid/melt}}$ data, to study the enrichment of W during fluid exsolution. Specifically, to test the reliability of the $D_{\text{fluid/melt}}$, the instantaneous W content of the exsolved fluid in the Xihuashan quartz-vein type W deposit was calculated and compared with that reported for fluid inclusion analyses.

2. Methods

2.1. Materials

The starting materials were synthetic anhydrous silicate glasses and Na$_2$WO$_4$ solutions. Synthetic anhydrous silicate glasses were prepared from analytical grade oxides (SiO$_2$ and Al$_2$O$_3$, prepared from analytical grade oxides (SiO$_2$ and Al$_2$O$_3$, decreasing the validity and accuracy of the obtained $D_{\text{fluid/melt}}$ values \cite{15}. It should be noted that fluid unmixing and loss of elements from silicate glass during quenching will further complicate the experimental results \cite{16}.

An HDAC was used as the high $T$–$P$ cell. The sample chamber of HDAC was constructed by a circular hole (500 μm in diameter) in the center of rhenium gasket (3000 μm in diameter and 250 μm in thickness) and two parallel diamond-anvil culets. In addition, a gas mixture of 97% argon +3% methane was flushing around the sample chamber to prevent the oxidation of diamonds and metallic parts. This allows in situ optical and spectroscopic observations of the sample within the cell at $T$–$P$ conditions approaching those at the lower crust and upper mantle (e.g., 3–5 GPa and 1000 °C \cite{25–27}). HDAC experiments were carried out at the State Key Laboratory for Mineral Deposits Research, Nanjing University.

The sample chamber was loaded with aqueous Na$_2$WO$_4$ solution, together with a bubble and a piece of silicate glass. To avoid the influence of evaporation on the Na$_2$WO$_4$ concentration during sample preparation, the aqueous solution within the sealed HDAC chamber was quantitatively analyzed using Raman spectroscopy (Text S1 online; Fig. S1 online). The starting solutions were 0.21–0.56 m Na$_2$WO$_4$. The compositions of the experimental systems were listed in Table 1 and Table S3 online.

The temperature of the sample chamber was controlled using Mo resistance heaters. The sample temperature was measured by two K-type thermocouples attached to the two diamond anvils (with an accuracy of ±2 °C). The pressure at a given temperature in the isochoric sample chamber of the HDAC was determined using the equation of state of the fluid system. Due to the lack of the equation of state for the Na$_2$WO$_4$ + H$_2$O system, the fluid composition was expressed as NaCl wt% (weight percent) equivalent, and the fluid pressure was calculated using the equation of state for the NaCl + H$_2$O system \cite{29}. Specifically, the fluid composition was calculated by melting temperature of ice in the NaCl + H$_2$O system \cite{30} and the density of the isochore was derived from the measured Aqueous (Aq) + Vapor (V) → Aq homogenization temperature ($T_0$) within the HDAC for that particular fluid composition. The Na$_2$WO$_4$ + H$_2$O + glass sample was first heated at a rate of 3 °C/min until the air bubbles (vapor phase, V) dissolved into the aqueous solutions (Aq) (i.e., the Aq + V → Aq homogenization; Fig. 1a, b). Then the sample was further heated to the designed temperatures at a rate of 5 °C/min. The $T_0$ (Aq + V → Aq) was measured again at the end of each run, which shows an acceptable variation (<5 °C) compared with those measured during the first heating, indicating a nearly constant sample volume.

2.2. Hydrothermal diamond-anvil cell (HDAC)

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2.3. Raman spectroscopic analyses

In situ Raman spectra of melt and fluid phases were acquired using a LabRam HR800 (Horiba Jobin Yvon) spectrometer hosted at the State Key Laboratory for Mineral Deposits Research, Nanjing University. The wavelength of the Nd:YAG excitation laser is 532 nm and the output power is 500 mW. The laser was focused on the fluid or melt sample through a 50× Olympus super long working distance objective. The laser output from the objective was ~100 mW in intensity. A 600 groove/mm grating was applied, and the spectral resolution was ~2 cm$^{-1}$.

The wavenumbers for all spectra ranged from 100 to 4000 cm$^{-1}$, which covers the typical vibration modes of tungstates, aluminosilicates, and water. The spectra were acquired for 20–60 s with 10 accumulations. At the beginning of each experiment, the spectrometer was calibrated using the 520.7 cm$^{-1}$ band of silicon. The Intensity Correction System (ICS) was applied to correct the intensity of all spectra. The influences of wavenumber and temperature on the spectral intensity were also corrected following the procedures described in Schmidt and Seward \cite{31}, Wang et al. \cite{32}, and Qiu et al. \cite{33}. All the corrected spectra were processed using the PeakFit v4 software.
Table 1
Experimental $T$–$P$–$x$ conditions, and species and $D_{\text{fluid/melt}}^{W}$ of tungsten during fluid exsolution.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$P$ (GPa)</th>
<th>H$_2$O (wt%)</th>
<th>Fraction and concentration of W species in fluid phase</th>
<th>Fraction and concentration of W species in melt phase</th>
<th>$D_{\text{fluid/melt}}^{W}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>mWO$_4$ (mol%)</td>
<td>mWO$_4$ (mol/kg H$_2$O)</td>
<td>mHWO$_4$ (mol%)</td>
</tr>
<tr>
<td>Run G0.73–1, 0.21 mol/kg Na$_2$WO$<em>4$ + G0.73 glass; ASI = 0.73; $T_h$ = 335 °C; $T</em>{\text{melt}}$ = 694 °C</td>
<td>700</td>
<td>0.35</td>
<td>10.07</td>
<td>0.1362</td>
<td>33.37</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>0.44</td>
<td>11.99</td>
<td>0.0539</td>
<td>73.04</td>
</tr>
<tr>
<td>Run G0.73–2, 0.56 mol/kg Na$_2$WO$<em>4$ + G0.73 glass; ASI = 0.73; $T_h$ = 221 °C; $T</em>{\text{melt}}$ = 692 °C</td>
<td>700</td>
<td>0.71</td>
<td>20.57</td>
<td>0.3010</td>
<td>44.29</td>
</tr>
<tr>
<td></td>
<td>725</td>
<td>0.75</td>
<td>20.98</td>
<td>0.2876</td>
<td>46.41</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>0.79</td>
<td>21.21</td>
<td>0.2848</td>
<td>46.29</td>
</tr>
<tr>
<td></td>
<td>775</td>
<td>0.82</td>
<td>21.30</td>
<td>0.2893</td>
<td>45.33</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>0.86</td>
<td>21.28</td>
<td>0.2688</td>
<td>49.07</td>
</tr>
<tr>
<td>Run G1.17–1, 0.54 mol/kg Na$_2$WO$<em>4$ + G1.17 glass; ASI = 1.17; $T_h$ = 210 °C; $T</em>{\text{melt}}$ = 695 °C</td>
<td>700</td>
<td>0.90</td>
<td>24.50</td>
<td>0.2241</td>
<td>56.22</td>
</tr>
<tr>
<td></td>
<td>725</td>
<td>0.94</td>
<td>26.64</td>
<td>0.1318</td>
<td>73.61</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>0.99</td>
<td>24.57</td>
<td>0.0747</td>
<td>85.07</td>
</tr>
<tr>
<td></td>
<td>775</td>
<td>1.03</td>
<td>24.34</td>
<td>0.0773</td>
<td>84.46</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>1.08</td>
<td>24.00</td>
<td>0.0558</td>
<td>88.46</td>
</tr>
</tbody>
</table>

a) The solubilities of H$_2$O in melt calculated following Ghiorso and Gualda [28]; b) the initial concentration of W in aqueous solutions at 21 °C, which was determined by Raman spectroscopy (Text S1 online); c) the aluminum saturation index (ASI) = 0.73, which was calculated by the mole ratio of Al$_2$O$_3$/(Na$_2$O + K$_2$O + CaO); d) the Aq + V $\rightarrow$ Aq homogenization temperature ($T_h$) of the Na$_2$WO$_4$ solutions within HDAC; e) the complete melting temperature ($T_{\text{melt}}$) of the glass.

Fig. 1. Phase behavior of Na$_2$WO$_4$ + H$_2$O + glass system (Run G0.73–1) in HDAC during heating. (a) Initial sample contains 0.21 m Na$_2$WO$_4$ solution (Aq), an air bubble (V), and a glass (G) at 21 °C; (b) V was homogenized into the Aq at 335 °C and 0.013 GPa; (c) partial melting of glass at 668 °C and 0.32 GPa; (d) complete melting of glass at 694 °C and 0.34 GPa, resulting in the coexistence of melt (M) and aqueous fluid; (e) the melt-fluid boundary faded away at 787 °C and 0.43 GPa, forming a metastable fluid phase; (f) the metastable fluid phase was separated into immiscible melt and fluid phases at higher $T$ and $P$. 

3. Results

3.1. Phase behavior at elevated T–P conditions

The experimental T–P and composition (x) conditions are summarized in Table 1 and Table S3 (online). For the experimental run of G0.73–1, 0.21 m Na2WO4 solution and a piece of silicate glass with ASI = 0.73 was heated to 800 °C (with a maximum pressure of 0.44 GPa) along the isochore of 0.74 g/cm³ (>335 °C). For run G0.73–2, silicate glass (ASI = 0.73) and 0.56 m Na2WO4 were heated along the isochore of 0.96 g/cm³ (>221 °C) up to 800 °C with a maximum pressure of 0.86 GPa. For run G1.17–1, 0.54 m Na2WO4 and a piece of glass with ASI = 1.17 were heated up to 800 °C with a maximum pressure of 1.08 GPa.

Fig. 1 shows the phase behavior within the HDAC during heating of run G0.73–1. The air bubble was homogenized into the aequous solution at 335 °C (Fig. 1a, b; Tn = 335 °C). Upon further heating, the glass (G) began to melt partially (Fig. 1c) and then completely at 694 °C (Fig. 1d). The melt droplets coalesced and the boundary between melt and fluid phases faded away at ~787 °C (Fig. 1e), indicating a near critical homogenization. However, this is not a supercritical fluid because the homogeneous phase was separated into immiscible melt and fluid phases at higher T–P conditions (Fig. 1f), indicating that the bulk sample composition was close to that of a supercritical fluid. The phase behaviors were similar in runs G0.73–2 and G1.17–1 except for the absence of the metastable homogeneous fluid phase shown in Fig. 1e.

3.2. In situ Raman spectroscopic characterization

In situ Raman spectra for experimental runs G0.73–2 (Fig. 2a) and G1.17–1 (Fig. 2b) are shown to describe the spectroscopic characteristics of the investigated fluid and melt phases.

3.2.1. Fluid phase

At room temperature, the main Raman bands of the fluid phase were observed at ~324, ~834, ~930, and 2700–3850 cm⁻¹. The ~930 cm⁻¹ band shifted to lower wavenumbers and became broader with increasing T–P. At T ≥ 400 °C, a shoulder at ~950 cm⁻¹ appeared at the high-wavenumber side of the ~930 cm⁻¹ band. The intensity of the ~950 cm⁻¹ band increased with rising temperature (Fig. 2a). A new band at ~775 cm⁻¹ was identified at T > 100 °C (Fig. 2a, b); its Raman intensity increased and the wavenumber decreased with increasing T–P. In run G1.17–1, the ~950 cm⁻¹ band became the predominant fluid species at T ≥ 725 °C (Fig. 2b). In addition, the ~950 cm⁻¹ band also shifted slightly to lower wavenumber with rising T–P.

In the high-wavenumber range, a broad, asymmetric, and strong band at 2700–3850 cm⁻¹ can be identified at 21–800 °C (Fig. 2a). This broad band shifted to higher wavenumbers and became more symmetric with rising T–P. At T above 650 °C, the band shape and wavenumber kept nearly constant.

3.2.2. Melt phase

The low-wavenumber region of the melt phase is characterized by strong broad bands at ~500, ~800–1000, and ~1100 cm⁻¹ (Fig. 2a). In addition, under the same T–P conditions, the width of the 3000–3850 cm⁻¹ envelope in the melt is larger than that of the fluid phase, and the bands at ~930 and ~950 cm⁻¹ were weaker in the melt phase than those in the fluid phase. However, variations in the relative intensity, wavenumber, and width of the ~930 and ~950 cm⁻¹ bands with T and P are consistent with those in the fluid phase (Fig. 2a, b).

4. Discussion

4.1. Silicate species in melts and fluids

Strong bands at ~500, ~770, 800–1000, and ~1100 cm⁻¹ of melt phase at ≥700 °C are related to the aluminosilicate melt structure [34,35]. A silicate melt can be regarded as a network composed of internal connecting chains or polymers of Si–O tetrahedrons. Oxygen atoms in silicate melts can exist as bridging oxygen (BO, T–O–T, with T=Si, Al), nonbridging oxygen (NBO, T–O–M, M = Ca, Na, K, etc.), and free oxygen (e.g., O–M–O) [36,37]. In general, the number of bridging oxygen can reflect the polymerization degree of melts [36,37]. Thus, the structure of silicate melts can be described in terms of melt species (Qn species, where n denotes the number of bridging oxygen in silicate complex) [35,38].

In the melt phase, the strong band at ~500 cm⁻¹ (Fig. 2a) arises from the bending or rocking motion of bridging oxygen in the aluminosilicate melt (νb(Si–O–Si), Qn with n < 4) [34,35]. The weak band at ~770 cm⁻¹ (Figs. 2b and 3a) is ascribed to the symmetric stretching vibration of Si(OH)4 monomers (νs(Si–OH), Q0) [34,35]. νd(Si–OH) band was also observed in the fluid phase (Figs. 2a, b, and 3a). The broad band associated with silicates at 800–1000 cm⁻¹ can be described using two Gaussian + Lorentz components at ~850 and ~900 cm⁻¹ (Fig. 3a), which were ascribed to the Si–O–H stretching vibrations of Q1 and Q2 species, respectively [35,39,40]. A weak broad band at ~1100 cm⁻¹ was also detected in the melt phase (Fig. 2b); this band was assigned to the Si–O stretching vibrations in Q3 species [35,40].

The Q0 species of the melt was suggested to be influenced by the concentration of H2O at constant Al/(Al + Si) ratio [41]. Steele-MacInnis and Schmidt [42] pointed out that the predominance of Q0 species is typical for fluids with relatively low SiO2 concentrations (<7 mol%, mole fraction). The predominance of Qn in the fluid phase and the absence of Qn (n ≥ 1) species in runs G0.73–2 and G1.17–1 (Fig. 2) indicate that the investigated fluid phases were depleted in aluminosilicate. Therefore, the influence of dissolved silicate on the geochemical behavior of tungstate can be neglected. The fraction of Q0 was reported to increase with rising H2O content (>20 mol%) [41], whereas the fraction of polymerized species, Qd decreased [40]. However, the variations in the spectral intensities of Q0 at ~900 cm⁻¹ and Qd at ~1100 cm⁻¹ with rising T–P in Fig. 2b did not show an obvious correlation with the variation of water content in melts (Table 1).

4.2. H2O in melts and fluids

The 2700–3850 cm⁻¹ massifs in fluid and melt spectra (Fig. 2) were assigned to the OH stretching vibrations of H2O (νs(OH)) [43]. The presence of H2O can affect the disordered tetrahedral silicate network of melts according to the following reactions [40]:

\[
\text{H}_2\text{O}_{\text{molecul}}(\text{melt}) + \text{O}(\text{melt}) \rightarrow 2\text{OH (melt)}
\]

\[
\text{H}_2\text{O}_{\text{molecul}}(\text{melt}) + \text{T}–\text{O}–(\text{melt}) \rightarrow 2\text{T}–\text{OH (melt)}
\]

where H2O molecule is molecular water, O is the bridging oxygen of the silicate network, and OH is the structurally bound hydroxyl group in the melt.

Eq. (1) implies a simple and commonly proposed dissolving mechanism of H2O in silicate melts, and Eq. (2) shows the breakdown of bridging oxygen and the formation of NBOs. Eqs. (1) and (2) suggested that H2O can be dissolved into the silicate melt as H2O molecules and hydroxyl groups, with the latter being bonded to the silicate network to form T–OH bonds and M–OH complexes under high T–P conditions [35,44]. Thus, two subcomponents were
proposed to account for the broad $\nu_s(\text{OH})$ band (Fig. 3b; Table S3 online). The band at $<3450–3550$ cm$^{-1}$ is assigned to the OH stretching vibration of H$_2$O molecule (Figs. 2a and 3b) [45,46], and the band at $>3550$ cm$^{-1}$ is ascribed to the vibration of (T, M)--OH groups (Figs. 2a and 3b) [45,46]. This spectrum-processing procedure can represent the $\nu_s(\text{OH})$ band well under high $T$–$P$ conditions [45]. As observed in Fig. 2, the ratio of OH/H$_2$O molecule in the fluid and melt increased with rising $T$–$P$, which is consistent with the evolution of the $\nu_s(\text{OH})$ spectra reported in the hydrous silicate system [35,45,46].

4.3. Partitioning behavior of tungsten between fluid and melt

4.3.1. Tungsten species in melt and fluid

In the fluid phase, the bands at $\sim$324, $\sim$834, and $\sim$930 cm$^{-1}$ result from the bending vibration ($\nu_{2\beta\delta}(\text{O–W–O})$), the asymmetric vibration ($\nu_{3}(\text{O–W–O})$), and the symmetric stretching vibration ($\nu_{1}(\text{W}=\text{O})$) of WO$_4^{2–}$, respectively [47]. An additional strong band at $\sim$950 cm$^{-1}$ can be assigned to the symmetric stretching vibration of HWO$_4$ at $>500$ °C (Figs. 2 and 3) [19,20]. The formation of HWO$_4$ can be described as [48]:

![Fig. 2.](image-url)
WO$_4^{2-}$ + H$^+$ $\rightarrow$ HWO$_4^-$ \hspace{1cm} (3)

As shown in Figs. 2 and 3a, WO$_4^{2-}$ and HWO$_4^-$ are predominant tungsten species at $T$ up to 800 °C. In experimental runs G0.73–1 and G0.73–2, WO$_4^{2-}$ predominated over HWO$_4^-$ under the investigated $T$–$P$ conditions (Table 1 and Table S3 online). In experimental run G1.17–1, HWO$_4^-$ was the most important tungsten species at $T$ > 700 °C (Fig. 2b and Table 1). The increasing fraction of HWO$_4^-$ with rising temperature was predicted in our previous low-$T$ hydrothermal experiments (<400 °C) [19,20]. This was also supported by thermodynamic calculations. For example, Wood and Samson [2] reported that the equilibrium constant ($log K$) of Eq. (3) can reach 11.1 at 600 °C and 0.1 GPa. Thermodynamic modeling of scheelite solubility in hydrothermal fluids indicated that HWO$_4^-$ was the dominant tungsten species in low-chloride fluids at 600–800 °C and 0.2 GPa [49].

As shown in Figs. 2 and 3b, the major tungsten species in the melt phase were comparable with those in the coexisting fluid phase. At the fluid exsolution stage, the fraction of HWO$_4^-$ was obviously increased, especially in peraluminous melts. For example, the fraction of HWO$_4^-$ can reach 88 mol% in G1.17–1 melts at 800 °C and 1.08 GPa (Table 1). Our results indicate that W$^{VI}$ in silicate melts exists as a tetra-coordination [18], and is not directly incorporated into the melt tetrahedral structure [17].

4.3.2. Determination of $D_{\text{fluid/melt}}$

Colin et al. [24] corrected the spectral intensities of different sulfur species using the densities of fluid and melt. Then they used the corrected intensities to calculate the partition coefficient of sulfur between fluid and melt. In this case, the spectral acquisition conditions (e.g., acquisition time, laser power, and focal depth) needed to be exactly the same for a pair of fluid and melt phases. However, accurate control of these experimental parameters is not available sometimes. We used a new and simple approach to measure the partition coefficients of tungsten between fluid and melts (Text S2 online).

Raman integrated intensity of species $i$ is a function of Raman scattering cross section, numbers of molecules per unit volume, and some experimental and instrumental parameters (Text S2 online) [31,32]. Theoretically, all experimental and instrumental parameters should be consistent in the same spectrum [31,32]. Therefore, the influences of experimental and instrumental parameters on the spectral intensity could be eliminated using a reasonable internal reference. Here, we chose the $v_1$(OH) band as the internal reference. By assuming that the Raman scattering cross sections of WO$_4^{2-}$ and HWO$_4^-$ are the same both in the melt and fluid phases (Text S2 online; Fig. S2 online), then $D_{i}$ can be determined following the Nernst Distribution Law [50]:

$$D_{W}^{\text{fluid/melt}} = \frac{C_{\text{fluid}}}{C_{\text{melt}}} = \frac{(A/W)_{\text{fluid}}}{(A/W)_{\text{melt}}} \times M_{\text{H}_2\text{O}}^{\text{melt}}$$ \hspace{1cm} (4)

where $D_{i}^{\text{fluid/melt}}$ is defined as the ratio of the molar concentration of W between the aqueous phase ($C_{W}^{\text{fluid}}$, mol/kg H$_2$O) and melt phase ($C_{W}^{\text{melt}}$, mol/kg melt). $(A/W)_{\text{fluid}}$ and $(A/W)_{\text{melt}}$ are the ratios between Raman integrated intensity of tungsten (i.e., WO$_4^{2-}$ and HWO$_4^-$) and H$_2$O in aqueous and melt phases, respectively. $M_{\text{H}_2\text{O}}^{\text{melt}}$ is the solubility of H$_2$O in the melt (g/g melt), which was calculated following the procedures by Chiorsio and Guala [28] under corresponding T–P–X conditions. Obviously, it is unnecessary to control the acquisition time, laser power, focal depth, and other instrumental and experimental parameters on purpose, because they would be eliminated during the calculations of $(A/W)_{\text{fluid}}$ and $(A/W)_{\text{melt}}$ ratios. In addition, there were some overlaps among Q$^2$, Q$^3$, and tungstate in the $v_1$(W=O) vibration region (Fig. 3a). To reduce the influence of Q$^0$ species on the Raman intensity of $v_1$(W=O) bands, a curve baseline correction was applied (Fig. 3a).

The equilibrium state between the melt and coexisting fluid phase could be well determined by analyzing the relationship between experimental duration and the $(A/W)_{\text{fluid}}$ and $(A/W)_{\text{melt}}$ ratios. To test the equilibrium between melt and coexisting fluid phase, multiple spectra of the fluid and melt were recorded in 3.0 h under a fixed T–P condition. Results showed that the integrated intensity ratio between $v_1$(W=O) and $v_1$(O–H) bands of H$_2$O could reach a stable value (<3% in 1σ) in 0.5 h. Colin et al. [24] suggested that the error of $D_{\text{fluid/melt}}$ was mainly caused by the calculation of the integrated spectral intensities (~10%). In addition, the estimates of solubility of H$_2$O in the melt can give rise to additional uncertainties; our estimated uncertainty for this approach is ~5%. Therefore, the total uncertainties of the obtained
partition coefficients are ~11% in this study. Obviously, in situ Raman spectroscopic analyses in combination with the HDAC technique can be applied to quantitatively characterize the geochemical behavior of W in melts and fluids. All spectral parameters and the obtained $D_{W}^{\text{fluid/melt}}$ were listed in Table 1 and Table S3 (online). Results showed that WO$_4^-$ and HWO$_4^-$ were characterized by comparable partitioning behaviors, being strongly enriched in the fluid phase during exsolution. The total $D_{W}^{\text{fluid/melt}}$ ranged from 8.6 to 37.1 under the investigated $T$-$P$-$x$ conditions.

As shown in Fig. 4, the $D_{W}^{\text{fluid/melt}}$ data in this study are higher than most data obtained in quenching experiments, but are still consistent with those determined through analyses of natural samples and a few quenching experiments (Table S1 online). Audétat et al. [9] and Zajacz et al. [10] obtained the W concentration in the coexisting silicate melt and fluid inclusions of a series of polymetallic deposits. The calculated $D_{W}^{\text{fluid/melt}}$ ranges from 0.6 to 60 at elevated temperatures and pressures ($T = 670$–$710 \degree C$; $P = 0$ .1–0.19 GPa). The $D_{W}^{\text{fluid/melt}}$ values of this study are within the above $D_{W}^{\text{fluid/melt}}$ range, although the latter shows a large variation.

This difference might be ascribed to the different formation stages of the investigated fluid inclusions. Our following numerical modeling (Section 4.3.3) indicates that the instantaneous W concentrations in the exsolved fluids show large variations with the initial water and W contents in the melt, and the fraction of released fluid.

On the contrary, our $D_{W}^{\text{fluid/melt}}$ values are higher than most ex situ experimental results (Fig. 4)[1,11,53–56]. The samples of most ex situ experiments were loaded into precious metal capsules. Under elevated $T$–$P$ conditions, the continuous loss of elements into the precious metal (i.e., the alloy effect) resulted in a non-equilibrium system, leading to the scattering of the obtained $D_{W}^{\text{fluid/melt}}$ values [11,15,21]. For instance, the $D_{W}^{\text{fluid/melt}}$ of Ba obtained from quenching experiments were one to two orders of magnitude lower than those measured in HDAC experiments [21]. It should be noted that the sample chamber in this study was made of rhenium, which does not form alloy with W in the experimental $T$–$P$ ranges [15,57]. The synthetic fluid inclusion approach was proposed to avoid the influence of the alloy effect [12,57]. Applying this approach, Schmidt et al. [12] determined the $D_{W}^{\text{fluid/melt}}$ values (0.04–29.9) at 750 $\degree C$ and 0.2 GPa as a function of ASI (0.99–1.16) of the melt for NaCl + KCl ± HCl fluids. Obviously, our $D_{W}^{\text{fluid/melt}}$ values are comparable with those reported in Schmidt et al. [12]. Therefore, we tend to conclude that the difference between our $D_{W}^{\text{fluid/melt}}$ and those obtained in most ex situ experiments could be largely ascribed to the alloy effect. Differences in the compositions of fluid and melt, as well as the fugacity of oxygen ($fO_2$), might also be possible explanations for the scattering of the reported $D_{W}^{\text{fluid/melt}}$ values. However, relevant experimental investigations are limited and even contradictory. For example, the presence of HF was reported to decrease the $D_{W}^{\text{fluid/melt}}$ (0.37–1.00 in comparison to 2.80–4.10 in HF-free system) [51], whereas the $D_{W}^{\text{fluid/melt}}$ seems to be increased in the presence of NaF (0.04–0.20 in comparison with 0.07 in NaF-free system) [52]. The $fO_2$ values of quenched experiments were mainly controlled at the NNO buffer [12,51].

It should be noted that $D_{W}^{\text{fluid/melt}}$ was obviously decreased under elevated $T$–$P$ conditions (Table 1 and Fig. 4). This result indicates that fluid exsolution occurring at shallower depth is capable of generating more enriched W-mineralizing fluids. In addition, $D_{W}^{\text{fluid/melt}}$ is higher in peralkaline melt than that in peraluminous melt (Fig. 4). The peralkaline granites (ASI < 1) are characterized by high concentrations of REE, Y, Zr, Nb (Nb/Ta), Sn, Th, Be, Rh, and U, whereas the metaluminous and peraluminous granites (ASI > 1) are enriched in Sn, W, Nb, Ta, Rh, Cs, Be, and Li [58]. In this study, the glass compositions are typical of the two end members of the aforementioned granite. Our results showed that the $D_{W}^{\text{fluid/melt}}$ decreased with rising ASI values (Table 1), which is consistent with those obtained in ex situ experiments [12]. However, most

![Fig. 4. The partition coefficient of tungsten ($D_{W}^{\text{fluid/melt}}$) between hydrothermal fluid and granitic melt. Data plotted are from Table 1 and Table S1 (online).](image-url)
tungsten-bearing granites are peraluminous or metaluminous instead of peralkaline [3,59]. This might be ascribed to the low concentration of W in peralkaline granite [58]. On the contrary, the evolved granite is rich in W-Sn rare metals and volatiles [58], favoring the exsolution of large amounts of W-mineralizing fluids.

4.3.3. Modelling the partitioning of W during fluid exsolution

A physical model of fluid exsolution from convective magma was considered. Here two scenarios of fluid exsolution were considered. In the first scenario (Model 1: Fig. 5a, b), the mass of silicate melt was assumed to remain essentially constant during the separation of the fluid phase. In other words, fluid exsolution was completed before the start of crystallization. The second scenario (Model 2; Fig. 5c, d) assumed that crystallization and fluid exsolution occurred at the same time, while the concentration of water in the residual melt was constant. Considering most tungsten-bearing granites are peraluminous or metaluminous [3,59], only the partitioning behaviors of W in the melt with ASI of 1.17 were modeled. The mathematical approaches of Holland [63] were applied (Text S3 online). The W contents of W-bearing granites range from <10 to >100 ppm [6,61]. We assumed that the initial W concentration in peraluminous melts was 10 ppm in this modeling. The water contents in the melts were set at 2 wt%–10 wt% at 700–800 °C, based on previous experimental investigations [10,62].

As shown in Fig. 5, the W concentration in the exsolved fluid is a function of $\frac{D_W}{D_W^{\text{fluid/melt}}}$, the initial water content in the melt, and the fraction of exsolved water. In both models, the instantaneous and cumulative W contents in the separated fluids were generally higher during low $T$–$P$ exsolution (dotted versus solid curves). This is because $\frac{D_W}{D_W^{\text{fluid/melt}}}$ decreased with rising $T$–$P$ (Table 1 and Fig. 4).

For Model 1, the lower initial water content in the melt, the higher instantaneous W content of fluid was achieved (Fig. 5a). Along with fluid separation, the instantaneous W content of fluid showed an obvious decreasing trend. For example, if the melt initially contained 5 wt% water and the exsolution occurred at 700 °C and 0.90 GPa, the W content decreased from 166 to 115 ppm with the fraction of exsolved water ranging from 10% to 50% (Fig. 5a and Table S4 online). For Model 2, when initial H$_2$O content in melts were 2 wt% and 5 wt%, variations in the instantaneous W content were different from those predicted in Model 1. That is the instantaneous W content increased slightly with a rising fraction of separated solution during low degree fluid exsolution but increased sharply at an elevated exsolution degree (e.g., >0.8, Fig. 5c). Large variations in the instantaneous W concentration of exsolved fluids might explain the wide W concentration range in natural fluid inclusions (e.g., from <10 to >1000 ppm) [10], because hydrothermal W-mineralization could occur during multiple charges of magmatic-hydrothermal fluids. In summary, the results of Model 2 suggest that W can be extracted continuously during the crystallization, and late-stage exsolution can form highly concentrated W-mineralizing fluids.

On the contrary, the cumulative W content always increases with rising initial water content in melt and the increasing fraction of exsolved water in both models, indicating that fluid exsolution is an important and efficient mechanism for the enrichment of W. For example, if half of fluid was separated from the peraluminous melt (initially contains 5 wt% H$_2$O at 700–800 °C, 0.9–1.08 GPa; Fig. 5b, d; Table S4 online), the cumulative W content in Model 1 could reach 486–578 ppm, which is >48 times higher than that in the primary peraluminous melt. However, the cumulative W content in Model 2 is enriched for 12–26 times under the same $T$–$P$ condition and the same exsolution degree. This enrichment efficiency makes...
the exsolved fluid capable of generating tungsten deposits, although the mineralization potential of granitic intrusions is not a simple function of the metal content in fluids [9].

Previous studies demonstrated that fractional crystallization could result in the enrichment of W in residual magmas [69,70,61,64]. Increases in volatile contents were reasonable during crystallization. Magma at mid- to deep-crustal levels (−20−35 km, 0.7−1.0 GPA) with −3 wt%−4.5 wt% water could evolve to a water-rich (−6 wt%−9 wt%) residual melt [65]. Under these conditions, the increase of H2O content could promote the removal of W from melt (Fig. 5a, c) and ultimately form a hydrothermal fluid with high cumulative W content (Fig. 5b, d). For example, the cumulative W content in exsolved hydrothermal fluid would be 2.2−3.9 times higher for peraluminous melt containing 10 wt% H2O than that with 2 wt% H2O if half of the fluid was released from the residual melt.

To further test the reliability of the experimental results, we used the obtained Dfluid/melt values to model the fluid exsolution for the W-bearing granite at the Xihuashan quartz-vein type wolframite deposit. The Xihuashan deposit (Jiangxi Province, South China) is spatially and temporally associated with Jurassic granitic rocks [66,67]. Whole rock analyses showed that the Xihuashan granitic melt were characterized by high contents of W (4.82−65.3 ppm), SiO2 (74.5 wt%−78.1 wt%), and total alkali (7.68 wt%−8.86 wt%), and the ASI was 1.01−1.16 [66,67]. Geochemical analyses indicated that the mineralizing fluids were exsolved from the highly fractionated granites [67]. The crystallization temperature of Xihuashan granitic melt was calculated to be 703 ± 28 °C based on the Ti-in-zircon thermometry [68]. Based on the above T−P−x conditions, we chose the Dfluid/melt value of 18.71 to simulate the fluid exsolving process (Table 1).

Yang et al. [69] described the fluid exsolution using a water saturated magmatic system. Here we adopted the same model [70] and applied the same parameters (except for the Dfluid/melt) as Yang et al. [69] to reconstruct the fluid exsolution process; the parameters include initial W concentration in melt (7.0 ppm), bulk crystal-melt partition coefficient of W (0.04−0.4), and solubility of H2O in melt (7.1 wt%) [69]. The calculated instantaneous W content in the released fluids ranged from 0 to 127 ppm, which was consistent with that obtained from LA-ICP-MS analyses of the fluid inclusions hosted in quartz (1−125 ppm) [69]. The difference is our results indicated that the instantaneous W content decreased with the increasing release of H2O, whereas Yang et al. [69] suggested that the instantaneous W content increased with increasing mass fraction of melt, or with increasing mass fraction of released H2O. Nevertheless, the above calculation indicated that the Dfluid/melt of this study could be used to describe the ore-forming process.

Overall, high water content in melt, high exsolution degree, and shallow exsolution depth are conducive to forming W-mineralizing fluids. This conclusion is consistent with the magma evolution and W-mineralization in South China [59,71]. Natural W-mineralizing fluids are generally characterized by complex compositions, including the presence of chlorides and volatile components (e.g., CO2, C, 0.90−1.08 GPa). Water-saturated peraluminous melts had higher Dfluid/melt (16.3−37.1) under similar T−P conditions.

Conflict of interest
The authors declare that they have no conflict of interest.

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Author contributions
Ye Qiu and Xiaolin Wang designed the experiment and wrote the manuscript with inputs from all other authors. Ye Qiu carried out the experiments under the supervision from Xiaolin Wang and Jianjun Lu. I-Ming Chou, Ye Wan, and Rui Sun contributed to the data analysis and modeling. Rongjing Zhang and Wenlan Zhang participated in discussions on the ore-forming process.

Appendix A. Supplementary materials
Supplementary materials to this article can be found online at https://doi.org/10.1016/j.scib.2022.10.024.


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