Research Article

Effects of pH and Salinity on the Hydrothermal Transport of Tungsten: Insights from In Situ Raman Spectroscopic Characterization of K₂WO₄-NaCl-HCl-CO₂ Solutions at Temperatures up to 400°C

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In situ Raman spectra of aqueous K₂WO₄-HCl, K₂WO₄-HCl-NaCl, and K₂WO₄-CO₂-NaCl solutions were collected at elevated temperature (T, 100–400°C) and constant pressure (P) of 30 MPa. The stretching vibration band of the W=O bond (ν₁) was analyzed to reveal the species of tungsten (W) responsible for the hydrothermal transport of W during mineralization. Results showed that monomeric tungstates with ν₁(W=O) bands at ~930 and 950 cm⁻¹ are the dominant W species in weakly alkaline (room temperature, pH = 7) to near-neutral (room temperature, pH = 7.2) solutions under the investigated T-P conditions. Overall, the stability of polymeric tungstate species with ν₁(W=O) bands at ~965–995 cm⁻¹ decreases with rising temperature and was not detected at ≥300°C in moderately acidic solution (room temperature, pH = 4.9). However, increased fluid acidity and salinity obviously enlarged the temperature stability field of polymeric tungstate species. In highly acidic solution (room temperature, pH = 1.4), polymeric tungstates are the only stable W species even at 400°C. In the presence of 1.9 mol/kg NaCl, polymeric tungstate(s) can persist to at least 350°C in moderately acidic solution. Considering that 300–350°C is the major W-mineralizing T range and W-mineralizing fluid is generally characterized by a moderately acidic nature, we propose that, in addition to monomeric tungstates, polymeric tungstates can also be important W species in some natural geological fluids that are responsible for the mineralization of W. Future studies of the W mineralization mechanism should take this issue into account.

1. Introduction

Tungsten (W) deposit is generally a typical hydrothermal deposit. Construction of the mechanism for the formation of hydrothermal deposit needs knowledge on the species of the element of interest in hydrothermal fluid. For example, the solubility of a mineral is in close association with the species of relevant elements, which in turn constrains the transport and precipitation of such elements (e.g., [1–3]). The hydrothermal W species is mainly derived from experimental investigation of WO₃ solubility (e.g., [4–6]). These research studies showed that W is mainly transported as monomeric tungstates (e.g., WO₄²⁻, HWO₄⁻, and H₂WO₄⁰⁻). However, tungstate tends to associate with each other to form polymeric tungstates, especially in acidic solutions (e.g., [7–12]). For instance, Wesolowski et al. [12] investigated
the stability of $\text{H}_2(\text{WO}_4)_6^{5-}$, $\text{H}_{10} (\text{WO}_4)_6^{2-}$, and $\text{H}_{18} (\text{WO}_4)_{12}^{6-}$ at temperatures from 95 to 290°C and suggested that polymeric tungstates are insignificant hydrothermal W species. Nevertheless, the fractions of the former two species increase with rising temperature at $\geq 200^\circ\text{C}$ [12]. Because W mineralization mainly occurs at a wide temperature range from 200 to 550°C [3, 13], information of the stability of such polymeric tungstates at higher temperatures ($\geq 290^\circ\text{C}$) should be carefully studied to improve our understanding of the transport and mineralization of W [3].

Compared with solubility [5, 6] and potentiometric [12] experiments, Raman spectroscopic analyses can provide more direct information on aqueous W species. Raman spectra of the symmetric stretching vibration of the W=O bond ($\nu_3$) provide important information of the molecular environment and can be used to identify various monomeric and polymeric tungstate species ([10, 11] and references therein). However, most Raman spectroscopic investigations of aqueous W species have been conducted at temperatures lower than that of the W mineralization (e.g., $< 200^\circ\text{C}$; [7, 8, 14–21]), which limits a better understanding of the hydrothermal transport of W. Recently, we investigated the W species in CO$_2$-bearing solutions at elevated temperatures ($T$) and pressures ($P$) through in situ Raman spectroscopic analyses [10, 11]. Our results showed that polymeric tungstates are responsible for the transport of W only at $< 300^\circ\text{C}$. At higher temperatures, monomeric tungstates are the dominant aqueous W species. Nevertheless, there are some aspects that should be further investigated.

Estimates of the acidity of the W-mineralizing fluids have been calculated mainly based on the muscovite-K feldspar equilibrium, which yields a fluid pH from 4 to 6 ([3, 22–25]). Accordingly, our previous experimental investigations were also focused on moderately acidic to weakly alkaline solutions [10, 11]. However, topaz has been reported to be in close association with W mineralization in some vein-type deposits, in addition to muscovite and K feldspar (e.g., [3, 26–29]). Thermodynamic calculation on the pH dependences of the speciation of aluminosilicates in hydrothermal fluids indicates that topaz remains stable at pH values significantly lower than that of the muscovite-K feldspar assemblage (Appendix A (available here)). Therefore, systematic experiments should be carried out to better address the effect of fluid pH on W species in hydrothermal fluids, especially in highly acidic fluids. In addition, fluid inclusion studies showed that W mineralization occurred in chloride-dominated solutions [3, 13]. The salinity ranges from less than 5 mass% to more than 50 mass% NaCl equiv. Nevertheless, the salinities of most W-mineralizing fluids are reported to be lower than 10 mass% NaCl equiv. (see Fig. 1 of [3]). Unfortunately, the effect of fluid salinity on the stability of different hydrothermal W species has rarely been discussed, with only a few exceptions (e.g., [12]). Then, investigations on the species of W in hydrothermal fluids must take the complex composition (x) nature of the W-mineralizing fluids into account.

We constructed high-pressure optical cells (HPOCs; [11, 30, 31]) containing aqueous K$_2$WO$_4$-HCl, K$_2$WO$_4$-HCl-NaCl, and K$_2$WO$_4$-CO$_2$-NaCl solutions with 0.01–0.03 mole/kg (m) tungstate. The major goal of this study is to investigate the influences of fluid acidity and salinity on the W species in hydrothermal fluids. To accomplish this, the specific objectives of this work are as follows: (1) collect high-resolution in situ Raman spectra of tungstate-bearing solutions in a wide temperature range from 100 to 400°C and at constant pressure of 30 MPa, especially in the presence of HCl and NaCl; (2) present the major hydrothermal W species under the investigated $T$-$P$-$x$ conditions; and (3) constrain the $T$-$P$-$x$ stability of the hydrothermal W species and discuss the hydrothermal transport and precipitation of W in the ore-forming systems.

### Table 1: Compositions of the sample solutions prepared at 22°C.

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<th>CO$_2$ concentration (m)</th>
<th>NaCl concentration (m)</th>
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<td></td>
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<td>0.76</td>
<td></td>
<td>1.90</td>
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</table>

$pH$ was measured at room temperature.

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### 2. Materials and Methods

#### 2.1. Optical and Spectroscopic Cells. Commercially available analytical grade reagents of K$_2$WO$_4$ (>99.5% purity, Aladdin Industrial Corporation), NaCl (>99.5% purity, Sigma-Aldrich Co., LLC), ~37 mass% HCl (Shanghai Lingfeng Chemical Reagent Co., Ltd.), and doubly deionized water were used to prepare aqueous solutions. The concentrations were reported in molality (mole/kg H$_2$O, m). As shown in Table 1, K$_2$WO$_4$ concentration ranges from 0.01 to 0.03 m. The HCl concentration ranges from 0.0003 to 0.15 m. The concentration of NaCl is ~1.9 m (10 mass%). The pH of these solutions was measured using a Mettler Toledo FE20 pH meter at room temperature; the measured pH ranges from 1.4 to 7.7. The prepared solutions were loaded into HPOCs [11, 30, 31], which were constructed from fused silica capillary tubing (Polymicro Technologies, LLC, http://polymicro.com). One end of a round cross-section fused silica capillary tubing with 600 $\mu$m outer diameter (OD), 200 $\mu$m inner diameter (ID), and about 16 cm long was sealed by fusion in an oxyhydrogen flame. The open end was cemented to the inside of a stainless steel high-pressure capillary tubing.
(1.59 mm OD, 0.76 mm ID, and 30 mm long). The prepared solution was sucked into a 1 mL syringe; one end of a thinner fused silica capillary tubing (50 μm ID, 150 μm OD, and ~25 cm long) was epoxied inside the syringe to replace the stainless steel needle. In this way, corrosion of the stainless steel needle and corresponding contamination of the fluid sample can be avoided during the loading of acidic solution. Then, the other end of the thinner silica tubing was inserted into the thicker silica tubing (i.e., 200 μm ID, 600 μm OD), and the solution was loaded into the HPOC through squeezing the syringe. Similarly, a section of mercury was loaded into the HPOC to separate the sample solution and the pressure medium (water in this study) using a modified syringe. Then, the HPOC was connected to a pressurization system. The fluid pressure was adjusted by a pressure generator and measured using an Omega PX91N0-35KSV digital pressure transducer with an Omega DP41-S-230 manometer (241 MPa full scale, accurate to ±0.5% of full scale or 1.2 MPa). The experimental setup was shown in Figure 1.

For the HPOC containing CO₂, the procedures of loading sample and measuring fluid composition were reported in Wang et al. [11]. The composition of this sample was also shown in Table 1.

### 2.2. Raman Spectroscopic Analyses

The temperature of HPOCs containing tungstate-bearing solutions was controlled by a Linkam CAP500 heating-cooling stage. The temperature of the stage was calibrated using the triple point (0°C) and boiling point (100°C) of water and the melting point of NaN₃ (306.8°C) at 0.1 MPa. The accuracy was reported to be ±0.1°C [32]. The investigated temperature range is 100–400°C. The pressure was maintained at 30 MPa. The fluid sample was kept at the target temperature for at least 2 h before in situ Raman spectroscopic analyses, to ensure the reaction equilibrium inside the HPOC.

Raman spectra were collected using a high-resolution Raman spectrometer (LabRAM HR800, Horiba Jobin Yvon). The wavelength of the air-cooled frequency-doubled Nd:YAG excitation laser is 532 nm. The laser power can be continuously adjusted from a few to 500 mW. In this study, the output power of the laser was set at 400 mW, allowing ~100 mW laser to reach the center of the horizontal HPOC. A 50x Olympus long working distance objective and a 1800 groove/mm grating with spectral resolution of approximately 1 cm⁻¹ were applied. The spectrometer was calibrated with the 520.7 cm⁻¹ peak of silicon. The spectra were collected from 800 to 1100 cm⁻¹ to cover the symmetric stretching vibration of the W=O bond in tungstate (v₁). Each spectrum was acquired for 300–800 s with three accumulations.

LabSpec 5.58.25 software was applied to process all the collected spectra. The baselines of the spectra were corrected with linear methods, and no smoothing was applied. For the overlapping v₁(W=O) peaks, the spectra were fitted using Gaussian+Lorentz functions. The integrated intensity or peak area (A) of different v₁(W=O) bands was used to calculate the fractions of different W species, based on the assumption that all the v₁(W=O) modes have equal scattering coefficients [11].

### 3. Results

#### 3.1. K₂WO₄-HCl-H₂O System

Figure 2 shows the in situ Raman spectra of K₂WO₄-HCl solutions with different pH at temperatures from 100 to 400°C. In HCl-free solution (initial pH = 7.7), the spectra are characterized by a strong v₁(W=O) band at ~930 cm⁻¹ (C₉₃₀, Figure 2(a)). With
increasing temperature, it shifts to a lower wavenumber. At >250°C, a new $v_1$ (W=O) band ($C_{956}$) at ~950 cm$^{-1}$ emerged. Peak area calculations showed that $C_{930}$ represents the dominant W species, with a peak area fraction of >92% (Figure 3(a); Table 2). In near-neutral solution (initial pH = 7.2), the spectra are similar with those for HCl-free weakly basic solution (Figures 2(a) and 2(b)). The only difference lies in that the additional $v_1$ (W=O) band at 965 cm$^{-1}$ ($C_{965}$) was observed at 100–150°C. The peak area fraction of $C_{965}$ was below 3% (Figure 3(b); Table 2). In moderately acidic solution (initial pH = 4.9), the situation is more complex (Figure 2(c)). At 100°C, the spectrum is characterized by two $v_1$ (W=O) bands, $C_{930}$ and $C_{965}$. With increasing temperature, $C_{965}$ disappeared and two new $v_1$ (W=O) bands at ~975 cm$^{-1}$ ($C_{975}$) and ~995 cm$^{-1}$ ($C_{995}$) were identified at 150–250°C. The peak area fractions of $C_{975}$ and $C_{995}$ reached a maximum of 4.8% and 24.1% at 200°C, respectively (Figure 3(c); Table 2). Then, their fractions started to decrease with rising temperature. $C_{956}$ was detectable at ≥250°C and became an important $v_1$ (W=O) band, along with $C_{930}$ at 300–400°C (Figure 3(c)). Unlike the former systems, $C_{930}$ and $C_{956}$ were not observed in highly acidic solution (initial pH = 1.4) (Figure 2(d)). At 100°C, the $v_1$ (W=O) band was characterized by a broad mas-sif ranging from 950 to 1010 cm$^{-1}$, which can be described using three formerly identified subbands of $C_{965}$, $C_{975}$, and $C_{995}$ (Figure 2(d)). $C_{965}$ vanished when temperature was increased to 150°C. At 150–350°C, the $v_1$ (W=O) spectra were characterized by $C_{975}$ and $C_{995}$. As shown in Figure 3(d), the peak area fraction of $C_{995}$ generally increased with rising temperature, whereas that of $C_{975}$ decreased. At 400°C, $C_{995}$ was the only observed $v_1$ (W=O) band.

**Figure 2:** *In situ* Raman spectra of the K$_2$WO$_4$-HCl-H$_2$O system at 100–400°C and 30 MPa. (a) Weakly alkaline solution with 0.03 m K$_2$WO$_4$ and initial pH of 7.7; (b) near-neutral solution with 0.03 m K$_2$WO$_4$+0.0003 m HCl and initial pH of 7.2; (c) moderately acidic solution with 0.02 m K$_2$WO$_4$+0.03 m HCl and initial pH of 4.9; and (d) highly acidic solution with 0.01 m K$_2$WO$_4$+0.15 m HCl and initial pH of 1.4.
3.2. $K_2WO_4\cdot HCl-NaCl-H_2O$ System. The in situ Raman spectra of $0.02 \, m \, K_2WO_4+0.03 \, m \, HCl+1.9 \, m \, NaCl$ were shown in Figure 4(a). The $C_{930}$ band was weak at low temperatures and became increasingly intensive at $\lesssim 300^\circ C$. At higher temperatures, its intensity decreased. The $C_{950}$ band was only observed at $\gtrsim 350^\circ C$. The intensity of the $C_{965}$ band generally decreased with increasing temperature and could not be detected at $\gtrsim 250^\circ C$. The $C_{975}$ band was observed at $200\sim 250^\circ C$ and disappeared at higher temperatures. $C_{995}$ occurred at $\gtrsim 200^\circ C$ and persisted to $350^\circ C$. Figure 4(b) shows the temperature dependence of the peak area fractions of these $v_1(W=O)$ bands. The fraction of $C_{995}$ increased slowly from 10.3% at $100^\circ C$ to 16.9% at $200^\circ C$ (Table 2). Then, it increased sharply to 69.2% at $300^\circ C$ and then started to decrease with rising temperature. For $C_{950}$, its fraction increased from 35.1% at $350^\circ C$ to 100% at $400^\circ C$ (Table 2). The fraction of $C_{965}$ showed a monotonic decrease from 93.3% at $100^\circ C$ to 86.8% at $200^\circ C$ and reached 0 at $\sim 230^\circ C$ (Table 2). The fraction of $C_{975}$ was the lowest among all the investigated $v_1(W=O)$ bands. Its maximum value is 12% at $250^\circ C$ and then decreased to 0 at $\sim 290^\circ C$ (Table 2). The fraction of $C_{995}$ increased to its maximum of 43.2% at $250^\circ C$ and then decreased to 11.5% at $350^\circ C$ (Table 2). The disappearance of this band possibly occurred at $\sim 380^\circ C$.

3.3. $K_2WO_4\cdot CO_2-NaCl-H_2O$ System. Figure 5(a) shows the spectra for $0.03 \, m \, K_2WO_4+0.76 \, m \, CO_2+1.9 \, m \, NaCl$ at 100 to $400^\circ C$ and at constant pressure of 30 MPa. At temperatures below $200^\circ C$, $C_{965}$, $C_{975}$, and $C_{995}$ were the major $v_1(W=O)$ bands. At $\gtrsim 200^\circ C$, the signal of $C_{990}$ became increasingly intense; $C_{930}$ and $C_{950}$ were the only observable $v_1(W=O)$ bands at $\gtrsim 350^\circ C$. $C_{995}$ was a major peak at $100\sim 300^\circ C$. Figure 5(b) further shows the peak area fractions of these $v_1(W=O)$ bands as a function of temperature and at constant pressure of 30 MPa. The peak area fraction of $C_{930}$ increased with rising temperature sharply at 150–300°C and then exhibited minor changes. For $C_{950}$, its fraction increased with increasing temperature at 300–350°C and then showed a slight decrease at higher temperature. The peak area fraction of $C_{965}$ generally decreased with rising temperature at 50–250°C and reached 0 at $\sim 270^\circ C$. The fraction of $C_{975}$ is 31.8% at $100^\circ C$ and then decreased to 0 at $\sim 290^\circ C$. The peak area fraction of $C_{995}$ also increased with rising temperature at lower temperature ($\lesssim 200^\circ C$) and decreased at higher

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**Figure 3:** Peak area fractions of different $v_1(W=O)$ bands as a function of temperature and at constant pressure of 30 MPa. (a) $0.03 \, m \, K_2WO_4+0.03 \, m \, HCl$; (b) $0.03 \, m \, K_2WO_4+0.0003 \, m \, HCl$; (c) $0.02 \, m \, K_2WO_4+0.03 \, m \, HCl$; and (d) $0.01 \, m \, K_2WO_4+0.15 \, m \, HCl$. It should be noted that the lines in the figure are used to show the general variation trend of the peak area fractions. Data plotted are those listed in Table 2.

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$C_i$, $A_i$, and $f_i$ represent, respectively, the peak position, the peak area, and the peak area fraction of the $\nu_1$ ($W=O$) band at wavenumber around $i$. 
temperature. However, it reached a maximum value of 51.3% at 200°C, which is higher than that of C975. At 300°C, this fraction decreased to 18% (Table 2). Extrapolating our results to higher temperature, the peak area fraction of C995 decreased to 0 at ~325°C.

4. Discussion

The transport of W in hydrothermal fluids has been intensively investigated, which can be roughly divided into two groups: (a) monomeric tungstates are the dominant W species in high-temperature fluids (e.g., >300°C; [3, 5, 6, 10, 11, 33]) and (b) polymeric tungstates are stable W species in low-temperature fluids, in addition to monomeric tungstates (e.g., <300°C; [7–12, 14, 15, 18, 34–36]). In the former case, the results were mainly derived from solubility experiments, which indicate that an increase in fluid acidity will favor the presence of H2WO4 and HWO4⁻ as the major W species, instead of WO4²⁻ [3]. In the latter case, Raman spectroscopic analyses have been proved to be a powerful method to study the aqueous W species (see Table 2 of [11]).
Previous Raman spectroscopic studies showed that the speciation of W is complex in acidic solutions at <200°C, mainly due to the presence of various polymeric tungstate species (e.g., [7, 9, 14, 20, 37]). Current assignments of the ν1 (W=O) bands were generally based on thermodynamic modeling (e.g., [9-11], and references therein). For the C$_{995}$ band, it has been unequivocally assigned to the W=O vibration in WO$_4^{2-}$ [9, 15, 17, 18, 20, 21, 36, 38]. The C$_{965}$ band was assigned to HWO$_4^−$ based on our previous investigations [11]. However, there is no generally accepted assignments of the high-wavenumber ν1 (W=O) bands (i.e., C$_{965}$, C$_{975}$, C$_{990}$, and C$_{995}$) to date (see Table 2 of [11]). Nevertheless, these ν1 (W=O) bands were all ascribed to the W=O vibration in polymeric tungstates. In fact, ab initio modeling might be helpful to describe the detailed structure of the polymeric tungstate species. Unfortunately, such modeling is not available at present. In this study, we tend to follow our previous assignments of the low-wavenumber ν1 (W=O) bands (C$_{930}$ and C$_{950}$) to monomeric tungstates and the high-wavenumber ν1 (W=O) bands (C$_{965}$—C$_{995}$) to polymeric tungstate species [10, 11].

4.1. Effect of Fluid Acidity on Tungsten Species. In weakly alkaline solutions, monomeric tungstates are the only (identified) W species (Figure 3(a)). This is in agreement with previous experimental and thermodynamic investigations [3, 9, 12]. In near-neutral solutions, polymeric tungstate is a minor species (<5%) in a narrow temperature range (70–200°C), and monomeric tungstates are still the dominant W species (Figure 3(b)). In moderately acidic solutions, polymeric tungstates are stable at <300°C (Figure 3(c)), which further supports our previous conclusions [10, 11]. Nevertheless, monomeric tungstates are still the major W species. In highly acidic solutions, polymeric tungstates are the only stable W species, even at high temperatures (i.e., 400°C; Figure 3(d)).

Most previous studies showed that polymeric tungstates are stable W species in acidic solutions at room temperature (e.g., [9, 14, 15, 20, 36]). A few experiments were focused on the stability of polymeric tungstates in hydrothermal fluids [7, 12]. In this work, studies of the effect of fluid acidity on the stability of aqueous W species, especially that of polymeric tungstate species, were extended to higher temperatures. For example, Bilal et al. [7] studied the aqueous speciation of W at ≤200°C and ≤100 MPa in weakly alkaline to moderately acidic solutions. Their results showed that monomeric tungstates are stable only in alkaline to weakly acidic solutions, and polymeric tungstates are the only stable aqueous W species in moderately acidic solutions. Our results support that the stability of polymeric tungstates increases with rising fluid acidity. However, in the investigated T-P conditions, monomeric tungstates are always the major aqueous W species in weakly alkaline to moderately acidic solutions (Figure 3(c)). Wesolowski et al. [12] investigated the stability of aqueous W species at ≤290°C using potentiometric method. They suggested that polymeric tungstates are not significant aqueous W species at high temperatures. However, their experiments showed that the stability of H$_7$(WO$_4$)$_6^{2−}$ and H$_{10}$(WO$_4$)$_5^{3−}$ increases with rising temperature at >200°C. On the contrary, our results indicate that, in moderately acidic solutions, the stability of all polymeric tungstates decreases with rising temperature at >200°C (Figure 3(c)). Increasing stability of some polymeric tungstate(s) is only observed at low temperatures in neutral to moderately acidic solutions (Figures 3(b) and 3(c)) or in highly acidic solution (Figure 3(d)).

4.2. Effect of Fluid Salinity on Tungsten Species. At constant K$_2$WO$_4$+HCl concentrations (Figures 3(c) and 4(b)), the presence of additional NaCl significantly increases the stability of polymeric tungstates. In particular, the fractions of polymeric tungstates are increased, and their stable T ranges shift to higher temperatures. For example, the fraction of C$_{995}$, the most stable polymeric tungstate species at higher temperatures, is estimated to be 24.1% in 0.02 m K$_2$WO$_4$+0.03 m HCl solution at 200°C (Figure 3(c); Table 2), while in 0.02 m K$_2$WO$_4$+0.03 m HCl+1.9 m NaCl solution, its fraction reaches 43.2% at 250°C and is still a stable W species at 350°C (Figure 4(b); Table 2). A similar phenomenon can also be observed in CO$_2$-bearing solutions (Figure 5). Our previous studies showed that W cannot associate with carbonate or bicarbonate to form carbonic tungstate species [10, 11]. The presence of CO$_2$ can increase the fluid acidity and favors the formation of polymeric tungstates at <300°C [10, 11]. However, the presence of additional NaCl obviously enlarges the stable T ranges of polymeric tungstate species (see Fig. 5(b) of [11] and Figure 5(b)). The fraction of C$_{995}$ is 18.0% at 300°C in 0.03 m K$_2$WO$_4$+0.76 m CO$_2$+1.9 m NaCl (Table 2), indicating that polymeric tungstate is still stable at ≥300°C.

The influence of salinity on aqueous W species has also been investigated for a long time. For example, the solubility of WO$_3$ was suggested to increase with rising fluid salinity [5, 6]. Consequently, the alkali tungstate ion pair was thought to be an important aqueous W species in hydrothermal fluids. However, this conclusion is not supported by some other experiment (e.g., [39]). The later experiment indicated a decrease in scheelite solubility with rising KCl concentration at constant temperature. Because solubility experiments were generally carried out at higher temperatures (e.g., >350°C; [5, 6]), the stability of polymeric tungstate(s) was not taken into account in these studies. Wesolowski et al. [12] studied the hydrolysis equilibrium of WO$_4^{2−}$ in hydrothermal fluids with NaCl concentrations ranging from 0.1 to 5.1 m. Although NaCl exerts insignificant influence on the stability of polymeric tungstates, an increase in NaCl concentration generally decreases the stability of certain polymeric tungstate (see Table IV of [12]). This is contrary to our experimental results, which indicate that polymeric tungstate species are more stable in the presence of additional NaCl in moderately acidic solutions.

In addition, our results also have implications for the study of the structure of aqueous polymeric tungstate species. Polymerization in acidic aqueous tungstate-bearing solutions has mainly been ascribed to the interaction among WO$_4^{2−}$ ions, and H$^+$ was also involved sometimes (see Table 2 in [11]). However, our results show that the presence of additional alkali cations (Na$^+$ in this study) obviously increases...
the stability of polymeric tungstates (Figures 3(c) and 4(b)). Previous studies suggested that Cl cannot complex with $\text{WO}_4^{2-}$ under hydrothermal conditions (e.g., [3, 5]). As a result, compared with $0.02 \text{ m} \ K_2\text{WO}_4+0.03 \text{ m} \ \text{HCl}$ solution, the increased fraction of polymeric tungstate species at high temperatures (e.g., $\geq 250^\circ \text{C}$) in $0.02 \text{ m} \ K_2\text{WO}_4+0.03 \text{ m} \ \text{HCl} +1.9 \text{ m} \ NaCl$ (Figures 3(c) and 4(b)) can only be ascribed to the increasing interaction between $\text{Na}^+$ and $\text{WO}_4^{2-}$, which forms complex polymeric tungstates. Then, future investigations on the structure of aqueous polymeric tungstates should take the interaction between alkali cation and tungstate anion into account.

4.3. Implications for the Hydrothermal Transport of Tungsten during Mineralization. Wood and Samson [3] summarized the geochemical characteristics of the W-mineralizing fluids. In general, the temperature, pressure, salinity, and pH are highly variable. The mineralizing temperature ranges from 200 to 500°C, with the interval from 300 to 350°C being the most important [40]. The fluid pressure ranges from a few to 160 MPa, while most W mineralization occurred at $<50 \text{ MPa}$. The fluid salinity covers a range from near 0 to $>55$ mass% NaCl equiv., whereas most W was deposited from a solution with salinity of $\leq 10$ mass% NaCl equiv. Estimate of the pH of W-mineralizing fluid is limited, and a moderately acidic solution with pH of 4–6 was proposed based on the muscovite-K feldspar equilibrium [3, 22–25]. Under the above conditions, W has been suggested to be transported in the forms of monomeric tungstates (i.e., $\text{H}_2\text{WO}_4^+$, $\text{HWO}_4^-$, $\text{WO}_4^{2-}$, $\text{MHWO}_4^0$, and $\text{MWO}_4^-$, where $M=\text{Na}^+$ or K$^+$) based on thermodynamic calculations (e.g., [3, 41]). However, our previous in situ Raman spectroscopic characterization of the $K_2\text{WO}_4+H_2O+CO_2$ system revealed that W can be transported as polymeric tungstates at $<300^\circ \text{C}$ [10, 11]. In the current study, the stable temperature field of polymeric tungstates in hydrothermal fluids was enlarged to at least 350°C, which covers the major W-mineralizing temperatures [3, 13, 40]. Therefore, polymeric tungstate species may also be responsible for the hydrothermal transport of W during W mineralization.

Maoping W deposit is located in the western Gannan W-Sn Metallogenic Province, which is the eastern part of the famous Nanling Metallogenic Belt of the South China Block [26, 42, 43]. Compared with other vein-type W deposits, topaz is a common gangue mineral in the early-stage wolframite-bearing veins, in addition to quartz and muscovite [26, 29]. In the late mineralizing stage, the amount of topaz is obviously decreased. According to our thermodynamic calculation (Appendix A), the muscovite-K feldspar-topaz assemblage indicates a more acidic solution than those for the muscovite-K feldspar equilibrium. In addition, fluid inclusion observations reveal a high temperature (up to 500°C) and high salinity (up to 19 mass% NaCl equiv.) W-mineralizing fluid in the early mineralizing stage [29]; CO$_2$ is a common volatile in this fluid. Late-stage quartz-hosted fluid inclusions yield homogenization temperature of $\leq 360^\circ \text{C}$ [26]. The fluid salinity is generally $<8$ mass% NaCl equiv., and CO$_2$ is not a common volatile in these fluid inclusions [26]. In summary, the early W-mineralizing fluid in Maoping W deposit is characterized by high temperature, high salinity, and strong acidity. With the process of W mineralization, the fluid temperature, salinity, and acidity were all decreased. Detailed mechanisms include natural cooling, CO$_2$ effervescence, and fluid mixing (e.g., [26, 27, 29]).

Based on our observations, W was mainly transported as monomeric tungstate species during the early-stage (e.g., $>400^\circ \text{C}$) mineralization in Maoping. At lower temperatures ($<400^\circ \text{C}$), polymeric tungstates contributed to the transport and deposition of W. The CO$_2$ effervescence was suggested to occur at $\sim 360^\circ \text{C}$ [27], which can decrease the fluid acidity. Greisenization along the quartz veins also consumed the hydrogen in the W-mineralizing fluid, resulting in an increase in fluid pH. However, the W-mineralizing fluid in Maoping could maintain its acidic nature throughout the mineralization. The major evidences include the following. (a) The occurrence of calcite has rarely been reported for the Maoping deposit [26, 27, 29, 43]. Calcite is often reported to be a late-stage gangue mineral resulting from the increased fluid pH (e.g., [40, 44]). CO$_2$ was also observed in late-stage quartz-hosted fluid inclusions, although its amount is much smaller than that in the early-stage topaz-hosted fluid inclusions [26, 29]. Then, carbonate/bicarbonate is available in the W-mineralizing fluid. The absence of calcite indicates a relatively low pH nature of the W-mineralizing fluid. (b) Topaz was observed throughout the W mineralization, although its amount was observed to decrease along with the mineralization. As calculated in Appendix A, topaz is indicative of an acidic hydrothermal fluid. In such moderately to highly acidic solution, polymeric tungstate is an important W species at $\leq 350^\circ \text{C}$ (Figures 3(c) and 4(b)). As shown in Fig. 10 of Legros et al. [28], LA-ICP-MS analyses of fluid inclusions hosted in topaz-bearing mineral assemblages generally yield an elevated W concentration, compared with that for topaz-free mineral assemblages. Therefore, the presence of polymeric tungstate(s) can maintain the high concentration of W in hydrothermal fluids, favoring high-grade W mineralization.

5. Conclusion

This study was mainly focused on the stability of different aqueous W species at elevated T-P conditions. Specifically, in situ Raman spectra of aqueous $K_2\text{WO}_4+\text{HCl}$, $K_2\text{WO}_4+\text{HCl}+\text{NaCl}$, and $K_2\text{WO}_4+\text{CO}_2+\text{NaCl}$ solutions were collected at 100–400°C and at constant pressure of 30 MPa, and the $\nu_1$ ($W=O$) bands were analyzed to investigate the species of W responsible for the hydrothermal transport of W. The major contributions are the following:

1. The effect of fluid acidity on the stability of hydrothermal W species was investigated. In weakly alkaline to near-neutral solutions, monomeric tungstates ($\nu_1$ ($W=O$) bands at 930 and 950 cm$^{-1}$) are always the predominant aqueous W species under the investigated T-P conditions. Polymeric tungstates ($\nu_1$ ($W=O$) bands range from 965 to 995 cm$^{-1}$) are stable only in acidic solutions, and their fractions
on the assignments of the Sciences. We thank Dr. Christian Schmidt (GFZ Program (QYZDY-SSW-DQC008) of Chinese Academy of Sciences, Grant nos. 41830428, and 41773036) and the Key Frontier Science Foundation of China (Grant nos. 41922023, 41820402, and 41922023). The authors declare that they have no conflicts of interests. All the experimental data are included in the text. Data Availability

All the experimental data are included in the text.

Conflicts of Interest

The authors declare that they have no conflicts of interests. Acknowledgments

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Thermodynamic modeling of the stability of aluminosilicate phases at varying fluid pH. (Supplementary Materials)

References


