Research Article

Effects of pH and Salinity on the Hydrothermal Transport of Tungsten: Insights from *In Situ* Raman Spectroscopic Characterization of K_2WO_4 -NaCl-HCl- CO_2 Solutions at Temperatures up to 400°C

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In situ Raman spectra of aqueous K_2WO_4 -HCl, K_2WO_4 -HCl-NaCl, and K_2WO_4 - CO_2 -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 (ν_1) was analyzed to reveal the species of tungsten (W) responsible for the hydrothermal transport of W during mineralization. Results showed that monomeric tungstates with ν_1 (W=O) bands at ~930 and 950 cm^{-1} are the dominant W species in weakly alkaline (room temperature, pH = 7.7) to near-neutral (room temperature, pH = 7.2) solutions under the investigated T - P conditions. Overall, the stability of polymeric tungstate species with ν_1 (W=O) bands at ~965–995 cm^{-1} decreases with rising temperature and was not detected at $\geq 300^\circ C$ 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 WO_3 solubility (e.g., [4–6]). These research studies showed that W is mainly transported as monomeric tungstates (e.g., WO_4^{2-} , HWO_4^- , and $H_2WO_4^0$). 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

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

Fluid system	W concentration (<i>m</i>)	HCl concentration (<i>m</i>)	CO ₂ concentration (<i>m</i>)	NaCl concentration (<i>m</i>)	pH ^a
K ₂ WO ₄ -H ₂ O	0.03				7.7
	0.03	0.0003			7.2
K ₂ WO ₄ -HCl-H ₂ O	0.02	0.03			4.9
	0.01	0.15			1.4
K ₂ WO ₄ -HCl-NaCl-H ₂ O	0.02	0.03		1.90	
K ₂ WO ₄ -CO ₂ -NaCl-H ₂ O	0.03		0.76	1.90	

^apH was measured at room temperature.

the stability of $\text{H}_7(\text{WO}_4)_6^{5-}$, $\text{H}_{10}(\text{WO}_4)_6^{2-}$, 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 >200°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 (>290°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 (ν_1) 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°C; [7, 8, 14–21]), which limits a better understanding of the hydrothermal transport of W. Recently, we investigated the W species in CO₂-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°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 K₂WO₄-HCl, K₂WO₄-HCl-NaCl, and K₂WO₄-CO₂-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.

2. Materials and Methods

2.1. Optical and Spectroscopic Cells. Commercially available analytical grade reagents of K₂WO₄ (>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 H₂O, *m*). As shown in Table 1, K₂WO₄ 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 μm outer diameter (OD), 200 μm 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

FIGURE 1: A schematic diagram showing the experimental setup. The lower part is a photo of a prepared HPOC containing sample solution, mercury, and pressure medium (water in this study).

(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 $\pm 0.5\%$ of full scale or 1.2 MPa). The experimental setup was shown in Figure 1.

For the HPOC containing CO_2 , 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 NaNO_3 (306.8°C) at 0.1 MPa. The accuracy was reported to be $\pm 0.1^\circ\text{C}$ [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 (ν_1). 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 $\nu_1(\text{W=O})$ peaks, the spectra were fitted using Gaussian+Lorentz functions. The integrated intensity or peak area (A) of different $\nu_1(\text{W=O})$ bands was used to calculate the fractions of different W species, based on the assumption that all the $\nu_1(\text{W=O})$ modes have equal scattering coefficients [11].

3. Results

3.1. $\text{K}_2\text{WO}_4\text{-HCl-H}_2\text{O}$ System. Figure 2 shows the *in situ* Raman spectra of $\text{K}_2\text{WO}_4\text{-HCl}$ 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 $\nu_1(\text{W=O})$ band at $\sim 930\text{ cm}^{-1}$ (C_{930} , Figure 2(a)). With

FIGURE 2: *In situ* Raman spectra of the K_2WO_4 -HCl- H_2O system at 100–400 °C and 30 MPa. (a) Weakly alkaline solution with 0.03 m K_2WO_4 and initial pH of 7.7; (b) near-neutral solution with 0.03 m K_2WO_4 +0.0003 m HCl and initial pH of 7.2; (c) moderately acidic solution with 0.02 m K_2WO_4 +0.03 m HCl and initial pH of 4.9; and (d) highly acidic solution with 0.01 m K_2WO_4 +0.15 m HCl and initial pH of 1.4.

increasing temperature, it shifts to a lower wavenumber. At $>250^\circ\text{C}$, a new $\nu_1(\text{W}=\text{O})$ band (C_{950}) at $\sim 950\text{ cm}^{-1}$ 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 $\nu_1(\text{W}=\text{O})$ 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 $\nu_1(\text{W}=\text{O})$ bands, C_{930} and C_{965} . With increasing temperature, C_{965} disappeared and two new $\nu_1(\text{W}=\text{O})$ bands at $\sim 975\text{ cm}^{-1}$ (C_{975}) and $\sim 995\text{ cm}^{-1}$ (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_{950} was detectable at $\geq 250^\circ\text{C}$ and became an important $\nu_1(\text{W}=\text{O})$ band, along with C_{930} at 300–400 °C (Figure 3(c)). Unlike the former systems, C_{930} and C_{950} were not observed in highly acidic solution (initial pH = 1.4) (Figure 2(d)). At 100 °C, the $\nu_1(\text{W}=\text{O})$ band was characterized by a broad massif 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 $\nu_1(\text{W}=\text{O})$ 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 $\nu_1(\text{W}=\text{O})$ band.

FIGURE 3: Peak area fractions of different $\nu_1(W=O)$ bands as a function of temperature and at constant pressure of 30 MPa. (a) $0.03\text{ m K}_2\text{WO}_4$; (b) $0.03\text{ m K}_2\text{WO}_4 + 0.0003\text{ m HCl}$; (c) $0.02\text{ m K}_2\text{WO}_4 + 0.03\text{ m HCl}$; and (d) $0.01\text{ m K}_2\text{WO}_4 + 0.15\text{ m HCl}$. 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.

3.2. $\text{K}_2\text{WO}_4\text{-HCl-NaCl-H}_2\text{O}$ System. The *in situ* Raman spectra of $0.02\text{ m K}_2\text{WO}_4 + 0.03\text{ m HCl} + 1.9\text{ m NaCl}$ were shown in Figure 4(a). The C_{930} band was weak at low temperatures and became increasingly intensive at $\leq 300^\circ\text{C}$. At higher temperatures, its intensity decreased. The C_{950} band was only observed at $\geq 350^\circ\text{C}$. The intensity of the C_{965} band generally decreased with increasing temperature and could not be detected at $\geq 250^\circ\text{C}$. The C_{975} band was observed at $200\text{--}250^\circ\text{C}$ and disappeared at higher temperatures. C_{995} occurred at $\geq 200^\circ\text{C}$ and persisted to 350°C . Figure 4(b) shows the temperature dependence of the peak area fractions of these $\nu_1(W=O)$ bands. The fraction of C_{930} increased slowly from 10.3% at 100°C to 16.9% at 200°C (Table 2). Then, it increased sharply to 69.2% at 300°C and then started to decrease with rising temperature. For C_{950} , its fraction increased from 35.1% at 350°C to 100% at 400°C (Table 2). The fraction of C_{965} showed a monotonic decrease from 93.3% at 100°C to 86.8% at 200°C and reached 0 at $\sim 230^\circ\text{C}$ (Table 2). The fraction of C_{975} was the lowest among all the investigated $\nu_1(W=O)$ bands. Its maximum value is 12% at 250°C and then decreased to 0 at $\sim 290^\circ\text{C}$ (Table 2). The fraction of C_{995} increased to its maximum of 43.2% at

250°C and then decreased to 11.5% at 350°C (Table 2). The disappearance of this band possibly occurred at $\sim 380^\circ\text{C}$.

3.3. $\text{K}_2\text{WO}_4\text{-CO}_2\text{-NaCl-H}_2\text{O}$ System. Figure 5(a) shows the spectra for $0.03\text{ m K}_2\text{WO}_4 + 0.76\text{ m CO}_2 + 1.9\text{ m NaCl}$ at 100 to 400°C and at constant pressure of 30 MPa. At temperatures below 200°C , C_{965} , C_{975} , and C_{995} were the major $\nu_1(W=O)$ bands. At $\geq 200^\circ\text{C}$, the signal of C_{930} became increasingly intense; C_{930} and C_{950} were the only observable $\nu_1(W=O)$ bands at $\geq 350^\circ\text{C}$. C_{995} was a major peak at $100\text{--}300^\circ\text{C}$. Figure 5(b) further shows the peak area fractions of these $\nu_1(W=O)$ 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 $150\text{--}300^\circ\text{C}$ and then exhibited minor changes. For C_{950} , its fraction increased with increasing temperature at $300\text{--}350^\circ\text{C}$ and then showed a slight decrease at higher temperature. The peak area fraction of C_{965} generally decreased with rising temperature at $50\text{--}250^\circ\text{C}$ and reached 0 at $\sim 270^\circ\text{C}$. The fraction of C_{975} is 31.8% at 100°C and then decreased to 0 at $\sim 290^\circ\text{C}$. The peak area fraction of C_{995} also increased with rising temperature at lower temperature ($\leq 200^\circ\text{C}$) and decreased at higher

TABLE 2: Fitting results of the *in situ* Raman spectra of the ν_1 ($W=O$) bands in the systems of $K_2WO_4-H_2O$, $K_2WO_4-H_2O-HCl$, $K_2WO_4-H_2O-HCl-NaCl$, and $K_2WO_4-H_2O-CO_2-NaCl$ at 100–400 °C and 30 MPa.

0.03 m K_2WO_4											
T (°C)	C_{930} (cm^{-1})	A_{930}	f_{930} (%)	C_{950} (cm^{-1})	A_{950}	f_{950} (%)	C_{965} (cm^{-1})	A_{965}	f_{965} (%)	C_{975} (cm^{-1})	A_{975}
100	931.9	113631	100.0				929.9	194229	98.5		
150							928.4	201745	97.1		
200	929.5	95156	100.0				926.9	200187	100.0		
250	926.3	74530	100.0				924.9	282491	100.0		
300	923.3	72424	98.2	951.4	1570	1.8	923.7	223324	90.0	952.2	24858
350	922.3	86219	95.5	951.7	4440	4.5	922.3	273629	90.2	951.6	29429
400	920.2	93418	92.2	951.2	7409	7.8	920.7	268387	91.5	952.4	24860
0.02 m $K_2WO_4+0.03m$ HCl											
T (°C)	C_{930} (cm^{-1})	A_{930}	f_{930} (%)	C_{950} (cm^{-1})	A_{950}	f_{950} (%)	C_{965} (cm^{-1})	A_{965}	f_{965} (%)	C_{975} (cm^{-1})	A_{975}
100	929.9	199250	73.1				962.9	73322	26.9		
150	927.8	252830	81.9				962.5	7718	2.5	975.5	7718
200	926.5	272797	71.1							976.0	18417
250	924.8	222967	75.0	950.7	27351	9.2				972.9	5351
300	923.4	103645	60.1	950.9	68809	39.9					
350	921.7	35724	44.3	950.8	44917	55.7					
370	921.0	49490	41.5	950.3	69763	58.5					
400	920.1	43839	47.0	949.9	49436	53.0					
0.01 m $K_2WO_4+0.15m$ HCl											
T (°C)	C_{930} (cm^{-1})	A_{930}	f_{930} (%)	C_{950} (cm^{-1})	A_{950}	f_{950} (%)	C_{965} (cm^{-1})	A_{965}	f_{965} (%)	C_{975} (cm^{-1})	A_{975}
100							963.5	23050	16.2	979.1	86117
150										977.3	18609
200										976.2	18022
250										972.0	8317
290										970.1	5835
350										968.4	1969
400										987.7	51891
0.02 m $K_2WO_4+0.03m$ HCl+1.90 m NaCl											
T (°C)	C_{930} (cm^{-1})	A_{930}	f_{930} (%)	C_{950} (cm^{-1})	A_{950}	f_{950} (%)	C_{965} (cm^{-1})	A_{965}	f_{965} (%)	C_{975} (cm^{-1})	A_{975}
100	929.5	6127	10.3				960.0	53084	93.3		
150	928.9	9234	13.2				959.5	60898	89.7		
200	926.3	23312	16.9				959.1	90277	86.8	975.3	3705
250	923.3	44700	44.8							974.6	11945
300	921.7	16312	69.2								
350	924.4	134460	53.4	949.5	88417	35.1					
400				950.6	18980	100.0					
0.03 m $K_2WO_4+0.0003m$ HCl											
T (°C)	C_{930} (cm^{-1})	A_{930}	f_{930} (%)	C_{950} (cm^{-1})	A_{950}	f_{950} (%)	C_{965} (cm^{-1})	A_{965}	f_{965} (%)	C_{975} (cm^{-1})	A_{975}
100							929.9	194229	98.5		
150							928.4	201745	97.1		
200							926.9	200187	100.0		
250							924.9	282491	100.0		
300							923.7	223324	90.0	952.2	24858
350							922.3	273629	90.2	951.6	29429
400							920.7	268387	91.5	952.4	24860
0.02 m $K_2WO_4+0.15m$ HCl											
T (°C)	C_{930} (cm^{-1})	A_{930}	f_{930} (%)	C_{950} (cm^{-1})	A_{950}	f_{950} (%)	C_{965} (cm^{-1})	A_{965}	f_{965} (%)	C_{975} (cm^{-1})	A_{975}
100							962.9	73322	26.9		
150							962.5	7718	2.5	975.5	7718
200										976.0	18417
250										972.9	5351
300											
350											
370											
400											
0.01 m $K_2WO_4+0.15m$ HCl											
T (°C)	C_{930} (cm^{-1})	A_{930}	f_{930} (%)	C_{950} (cm^{-1})	A_{950}	f_{950} (%)	C_{965} (cm^{-1})	A_{965}	f_{965} (%)	C_{975} (cm^{-1})	A_{975}
100							963.5	23050	16.2	979.1	86117
150										977.3	18609
200										976.2	18022
250										972.0	8317
290										970.1	5835
350										968.4	1969
400										987.7	51891
0.02 m $K_2WO_4+0.03m$ HCl+1.90 m NaCl											
T (°C)	C_{930} (cm^{-1})	A_{930}	f_{930} (%)	C_{950} (cm^{-1})	A_{950}	f_{950} (%)	C_{965} (cm^{-1})	A_{965}	f_{965} (%)	C_{975} (cm^{-1})	A_{975}
100	929.5	6127	10.3				960.0	53084	93.3		
150	928.9	9234	13.2				959.5	60898	89.7		
200	926.3	23312	16.9				959.1	90277	86.8	975.3	3705
250	923.3	44700	44.8							974.6	11945
300	921.7	16312	69.2								
350	924.4	134460	53.4	949.5	88417	35.1					
400				950.6	18980	100.0					

TABLE 2: Continued.

0.03 m K ₂ WO ₄ +0.76 m CO ₂ +1.90 m NaCl															
<i>T</i> (°C)	<i>C</i> ₉₃₀ (cm ⁻¹)	<i>A</i> ₉₃₀	<i>f</i> ₉₃₀ (%)	<i>C</i> ₉₅₀ (cm ⁻¹)	<i>A</i> ₉₅₀	<i>f</i> ₉₅₀ (%)	<i>C</i> ₉₆₅ (cm ⁻¹)	<i>A</i> ₉₆₅	<i>f</i> ₉₆₅ (%)	<i>C</i> ₉₇₅ (cm ⁻¹)	<i>A</i> ₉₇₅	<i>f</i> ₉₇₅ (%)	<i>C</i> ₉₉₅ (cm ⁻¹)	<i>A</i> ₉₉₅	<i>f</i> ₉₉₅ (%)
100	933	7553	12.6				959.7	26452	44.1	974.8	19042	31.8	996.1	6925	11.5
150	929.5	802	1.2				961.2	25340	36.6	974.8	8692	12.6	994.5	34412	49.7
200	928.3	4694	9.2				960.6	16812	32.9	974.4	3340	6.5	993.2	26179	51.3
250	926.4	19075	38.9				957.2	7295	14.4	973.5	1954	3.9	991.8	21751	42.9
300	925.1	35511	68.6	951.5	6950	13.4							990.8	9291	18.0
350	924.5	47764	69.4	951.0	21050	30.6									
400	922.8	51554	72.5	952.8	19525	27.5									

C_i, *A_i*, and *f_i* represent, respectively, the peak position, the peak area, and the peak area fraction of the *ν*₁ (W=O) band at wavenumber around *i*.

FIGURE 4: (a) *In situ* Raman spectra of 0.02 m K_2WO_4 +0.03 m HCl+1.9 m NaCl solution at 100–400°C and 30 MPa; (b) peak area fractions of different $\nu_1(\text{W}=\text{O})$ bands as a function of temperature for the solution shown in (a). 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.

FIGURE 5: (a) *In situ* Raman spectra of 0.03 m K_2WO_4 +0.76 m CO_2 +1.9 m NaCl solution at 100–400°C and 30 MPa; (b) peak area fractions of different $\nu_1(\text{W}=\text{O})$ bands as a function of temperature for the solution shown in (a). 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.

temperature. However, it reached a maximum value of 51.3% at 200°C, which is higher than that of C_{975} . At 300°C, this fraction decreased to 18% (Table 2). Extrapolating our results to higher temperature, the peak area fraction of C_{995} 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 H_2WO_4^0 and HWO_4^- as the major W species, instead of WO_4^{2-} [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 $<200^{\circ}\text{C}$, mainly due to the presence of various polymeric tungstate species (e.g., [7, 9, 14, 20, 37]). Current assignments of the $\nu_1(\text{W}=\text{O})$ bands were generally based on thermodynamic modeling (e.g., [9–11], and references therein). For the C_{930} band, it has been unequivocally assigned to the $\text{W}=\text{O}$ vibration in WO_4^{2-} [9, 15, 17, 18, 20, 21, 36, 38]. The C_{950} band was assigned to HWO_4^- based on our previous investigations [11]. However, there is no generally accepted assignments of the high-wavenumber $\nu_1(\text{W}=\text{O})$ bands (i.e., C_{965} , C_{975} , C_{990} , and C_{995}) to date (see Table 2 of [11]). Nevertheless, these $\nu_1(\text{W}=\text{O})$ bands were all ascribed to the $\text{W}=\text{O}$ 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 $\nu_1(\text{W}=\text{O})$ bands (C_{930} and C_{950}) to monomeric tungstates and the high-wavenumber $\nu_1(\text{W}=\text{O})$ 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 $<300^{\circ}\text{C}$ (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 $\leq 200^{\circ}\text{C}$ 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 $\leq 290^{\circ}\text{C}$ 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 $\text{H}_7(\text{WO}_4)_6^{5-}$ and $\text{H}_{10}(\text{WO}_4)_6^{2-}$ increases with rising tempera-

ture at $>200^{\circ}\text{C}$. On the contrary, our results indicate that, in moderately acidic solutions, the stability of all polymeric tungstates decreases with rising temperature at $>200^{\circ}\text{C}$ (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_2WO_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 $0.02\text{ m K}_2\text{WO}_4$ + 0.03 m HCl solution at 200°C (Figure 3(c); Table 2), while in $0.02\text{ m K}_2\text{WO}_4$ + 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 $<300^{\circ}\text{C}$ [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 $0.03\text{ m K}_2\text{WO}_4$ + 0.76 m CO_2 + 1.9 m NaCl (Table 2), indicating that polymeric tungstate is still stable at $\geq 300^{\circ}\text{C}$.

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., $>350^{\circ}\text{C}$; [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 WO_4^{2-} under hydrothermal conditions (e.g., [3, 5]). As a result, compared with 0.02 *m* K_2WO_4 +0.03 *m* HCl solution, the increased fraction of polymeric tungstate species at high temperatures (e.g., $\geq 250^\circ\text{C}$) in 0.02 *m* K_2WO_4 +0.03 *m* HCl +1.9 *m* NaCl (Figures 3(c) and 4(b)) can only be ascribed to the increasing interaction between Na^+ and 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 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 ≤ 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., H_2WO_4^0 , HWO_4^- , WO_4^{2-} , MHW_4^0 , and MWO_4^- , where $\text{M} = \text{Na}^+$ or K^+) based on thermodynamic calculations (e.g., [3, 41]). However, our previous *in situ* Raman spectroscopic characterization of the K_2WO_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_2WO_4 +HCl, K_2WO_4 +HCl+NaCl, and K_2WO_4 + CO_2 +NaCl solutions were collected at 100– 400°C and at constant pressure of 30 MPa, and the ν_1 ($\text{W}=\text{O}$) 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 ($\nu_1(\text{W}=\text{O})$ bands at 930 and 950 cm^{-1}) are always the predominant aqueous W species under the investigated *T-P* conditions. Polymeric tungstates ($\nu_1(\text{W}=\text{O})$ bands range from 965 to 995 cm^{-1}) are stable only in acidic solutions, and their fractions

generally decrease with increasing temperature. The only exception is highly acidic solution, where polymeric tungstates are stable even at 400°C.

- (2) Fluid salinity exerts a positive effect on the stability of polymeric tungstates. In moderately acidic solution, which is typical of W-mineralizing fluid, the presence of NaCl obviously enlarges the stable T. range for polymeric tungstates. These W species can persist to at least 350°C indicating that polymeric tungstates are also important aqueous W species at elevated temperatures, in addition to monomeric tungstate species. In addition, our result suggests that future study of the structure of polymeric tungstates should take the interaction between alkali cations and tungstate anions into account.
- (3) Based on the commonly geochemical features of reported W-mineralizing fluids, we propose that polymeric tungstates are also responsible for the transportation of W under hydrothermal conditions, especially at $\leq 350^\circ\text{C}$. Accordingly, decreasing acidity and salinity of hydrothermal fluids will destabilize polymeric tungstates, resulting in the precipitation of W.

Data Availability

All the experimental data are included in the text.

Conflicts of Interest

The authors declare that they have no conflicts of interests.

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Supplementary Materials

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

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