Wolframite solubility and precipitation in hydrothermal fluids: insight from thermodynamic modeling

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Abstract: Wolframite, a solid-solution series between hübnerite (MnWO$_4$) and ferberite (FeWO$_4$), is the main tungsten-bearing ore mineral in vein-type tungsten deposits. Much progress has been made on characterizing the mineralizing fluids precipitating wolframite, but it remains poorly understood what are the mechanisms depositing wolframite effectively and the variables controlling Mn/Fe ratios in wolframite. This study examines chemical controls on wolframite solubility in hydrothermal fluids and Mn/Fe ratios in wolframite using thermodynamic models for fluids in the systems of W-Mn-Cl-Na-O-H and W-Fe-Cl-Na-O-H. The fluid-buffered models are established based on the characteristics of vein-type tungsten deposits. The modeling results indicate that solubilities of hübnerite and ferberite in hydrothermal fluids at typical W-mineralizing conditions ($300-400 \, ^\circ\text{C}$, $500-1500$ bars, $5-15$ wt. % NaCl equivalent, pH=4-6) reach up to hundreds of ppm. The predominant tungsten, manganese, and iron species in fluids are HWO$_4^-$, MnCl$_2^0$ and FeCl$_2^2$-, respectively. An increase in pH and a decrease in fluid temperature and salinity are efficient mechanisms precipitating hübnerite and ferberite from acidic hydrothermal fluids. Hübnerite and ferberite are also significantly dissolved in alkaline hydrothermal fluids, but their solubilities in alkaline fluids are insensitive to fluid temperature and salinity. This may affect W mineralization at stages with different pH levels (e.g. the greisen stage and the alkaline stage). The Mn/Fe
ratio of mineralizing fluids is the principal variable controlling Mn/Fe ratios in wolframite. More supply of Fe than Mn from the fertile magma tends to produce Fe-rich mineralizing fluids. This may be one of reasons why ferberite is more common than hübnerite in tungsten deposits and why hübnerite is more likely to precipitate at an early stage.

**Keywords:** tungsten deposits; wolframite; ferberite; hübnerite; thermodynamic model

1. Introduction

Tungsten mineralization is genetically related to highly fractionated granites and dominated by greisen, quartz-vein, skarn, and porphyry types (Černý et al., 2005; Huang and Jiang, 2014; Mao et al., 2013; Zhao et al., 2017). The main ore minerals in tungsten deposits are scheelite and wolframite (e.g. Brown and Pitfield, 2013; Gong, 2015; Harlaux et al., 2018; Lu et al., 2003; Rasmussen et al., 2011), the latter of which often occurs in vein-type tungsten deposits. Vein-type tungsten deposits account for approximately 44 % of known tungsten economic resources next to skarn tungsten deposits (48%) (Werner et al., 2014). Southern China hosts the most abundant vein-type tungsten deposits in the world (Liu and Ma, 1993; Zhao et al., 2017). Large-scale or clustered vein-type tungsten deposits were also exploited around the Mole Granite, Australia (Audétat et al., 2000b), in Panasqueira, Portugal (Foxford et al., 2000; Launay et al., 2018), in southwest England (Sanderson et al., 2008), in the Erzgebirge, Germany and the Czech Republic (Breiter et al., 1999; Štemprok et al., 1994), in the Variscan French Massif Central (Harlaux et al., 2017, 2018), and in the Iberian Massif, Spain (Garate-Olave et al., 2017; Llorens and Moro, 2012).
Wolframite, \((\text{Mn,Fe})\text{WO}_4\), is a solid-solution series between hübnerite \((\text{MnWO}_4)\) and ferberite \((\text{FeWO}_4)\) (e.g. Harlaux et al., 2018; Pačevski et al., 2007; Sakamoto, 1985; Tindle and Webb, 1989; Xie et al., 2017; Zhang et al., 2018b). Much progress has been made on characterizing the mineralizing fluids precipitating wolframite (e.g. Breiter et al., 2017; Campbell and Panter, 1990; Chen et al., 2018; Korges et al., 2017; Legros, 2018; Li et al., 2018b; Ni et al., 2015), but it is still poorly understood how much tungsten can dissolve in mineralizing fluids. The thermodynamic model developed by Wood and Samson (2000) put a quantitative constraint on ferberite solubility in hydrothermal fluids, but solubility of the other end-member hübnerite remains poorly constrained. Therefore, it is necessary to develop thermodynamic models that incorporate Mn species and reactions in NaCl aqueous solutions.

Wolframite shows variable Mn/Fe ratios either in a single crystal or at different depths of a tungsten deposit (e.g. Harlaux et al., 2018; Pačevski et al., 2007; Xie et al., 2017). The reasons for this phenomenon have been debated for many years (e.g. Amosse, 1981; Campbell, 1988; Hollister, 1970; Pačevski et al., 2007; Taylor and Hosking, 1970; Tindle and Webb, 1989). Some studies find correlation between the Mn/Fe ratios in wolframite and some variables (e.g. temperature, pH, and Mn/Fe ratio of mineralizing fluids) (Amossé, 1978; Hollister, 1970; Horner, 1979), while others do not support it (Buhl and Willgallis, 1984; Buhl and Willgallis, 1985; Moore and Howie, 1978; Nakashima et al., 1986). Ferberite is identified in many tungsten deposits of southern China (e.g. Xie et al., 2017; Zhang, 1981; Zhang et al., 2018a), at the Panasqueira deposit, Portugal (Lecumberri-Sanchez et al., 2017), in most tungsten deposits of the Variscan French Massif Central (Harlaux et al., 2018b).
2018), in some tungsten deposits of the Iberian Massif, Spain (Llorens and Moro, 2012), and in the tungsten deposits of central Rwanda (Goldmann et al., 2013). Hübnerite is rarer than ferberite (King, 2005), but it is reported to be the dominant tungsten-bearing mineral in some vein-type tungsten deposits (e.g. Casadevall and Rye, 1980; Frolova et al., 2014; Harlaux et al., 2018; Neiva, 2008; Tindle and Webb, 1989; Wu et al., 2017). Until now, it remains poorly understood what controls the wolframite solid-solution composition.

Chemical mass transfer modeling is a powerful tool for understanding the transport and deposition of metals in ore-forming hydrothermal systems (e.g. Gibert et al., 1992; Heinrich, 2005; Heinrich et al., 1996; Hofstra et al., 1991; Liu et al., 2018; Migdisov et al., 2019; Phillips and Evans, 2004; Sushchevskaya and Bychkov, 2010; Wood and Samson, 2000). In this study, thermodynamic models in the system of W-Mn-Cl-Na-O-H and W-Fe-Cl-Na-O-H were established to quantify wolframite solubility in NaCl solutions and identify the variables that may control Mn/Fe ratios in wolframite.

2. Geochemical characteristics of W-mineralizing fluids

Wood and Samson (2000) and Naumov et al. (2011) have summarized the geochemical parameters (e.g. temperature, pressure, and salinity) of W-mineralizing fluids, and most of those parameters are determined from opaque minerals (e.g. quartz, topaz, and cassiterite). The W-mineralizing fluids have homogenization temperatures from 200 to 400 °C (Naumov et al., 2011). Recent infrared microthermometric studies of fluid inclusions in wolframite suggest that the mineralization temperatures of tungsten deposits range from 300 to 400 °C (e.g. Chen et al., 2018; Li et al., 2018b; Ni et al., 2015; Pan et al., 2019). The
mineralization pressures fall in the range of 500-1500 bars and the fluid salinities are typically less than 10 wt. % NaCl equivalent (Naumov et al., 2011; Wood and Samson, 2000). Based on muscovite-K-feldspar equilibria, pH of mineralizing fluids is estimated to be at neutral to moderately acid levels (pH=4-6) (Polya, 1989; Seal et al., 1987; So et al., 1991; So and Yun, 1994). Recent laboratory experiments suggest that significant tungsten could also dissolve in alkaline aqueous fluids at 300-400 °C (Li et al., 2018a). The fluids’ oxygen fugacity commonly falls between quartz-fayalite-magnetite and hematite-magnetite buffers (e.g. Han et al., 2016; Jiang et al., 2004; Wood and Samson, 2000). CO\textsubscript{2}-bearing fluid inclusions are recently found in wolframite of a few tungsten deposits (e.g. Chen et al., 2018; Pan et al., 2019), but the CO\textsubscript{2} contents in those mineralizing fluids have not been precisely determined yet. Compiled data in Wood and Samson (2000) suggest that the mole fraction of CO\textsubscript{2} in fluid inclusions is typically between 0 and 0.1.

Recently reported in-situ compositions of fluid inclusions in tungsten deposits were compiled here to examine the relationship between W and other ore elements (e.g. Fe and Mn) and put a better constraint on thermodynamic modeling. The data sources include the Sn-W deposits around the Mole Granite, Australia (Audétat et al., 2000a), the Panasqueira tungsten deposit, Portugal (Lecumberri-Sanchez et al., 2017), the tungsten deposits in the Erzgebirge, Germany and the Czech Republic (Korges et al., 2017), and the Piaotang and Maoping tungsten deposits, China (Legros et al., 2019). Note that wolframite is the main ore mineral of those tungsten deposits.

Most W concentrations in fluid inclusions of those tungsten deposits have a range of a few to hundreds of ppm (Fig. 1a). The two tungsten deposits in China have the largest
average tungsten concentration (Fig. 1b). Both Fe and Mn are identified from fluid inclusions in the Sn-W deposits around the Mole Granite and the tungsten deposits in the Erzgebirge, while only Fe or Mn are found in the other tungsten deposits. The molality ratios of W against Fe and Mn range mainly from $10^{-4}$ to $10^{-1}$, and the W/Fe ratios are slightly lower than the W/Mn ratios on average (Fig. 2a). The W/(Fe+Mn) ratios fall into a wider range of $10^{-5}$ to 1 and peaks at $10^{-3}$ and $10^{-1}$ (Fig. 2b).

Wood and Samson (2000) employed stoichiometric dissolution of ferberite and scheelite ($\sum W = \sum Fe + \sum Ca$) as one of mass balance equations in their models. However, W concentrations in mineralizing fluids are generally a few orders of magnitude lower than Fe and Mn concentrations (Fig. 2). Constrained by the W/Fe ratios and W/Mn ratios of fluid inclusions above, the following two equations were used to replace stoichiometric dissolution of ferberite and hübnerite:

$$\sum W = \sum \frac{Mn}{\lambda}$$

(1)

$$\sum W = \sum \frac{Fe}{\lambda}$$

(2)

in which $\lambda$ ranges from 10 to 1000.

3. Species and reactions in fluid-buffered thermodynamic models

Two limiting cases of fluid-rock interactions in natural hydrothermal systems are fluid-buffered and rock-buffered (Heinrich, 1990). In the fluid-buffered case, chemical reactions are controlled entirely by equilibria among fluid species, while fluids are in equilibrium contact with excess rock in the rock-buffered case. Rock-buffered thermodynamic models are more applicable to skarn-type and greisens-type tungsten
deposits, which cannot be created without metasomatism (e.g. Gibert et al., 1992; Halter et al., 1998). The thermodynamic models for vein-type tungsten deposits in this study are fluid-buffered because high-efficiency tungsten mineralization in those deposits requires large fluid focusing and incomplete buffering of mineralizing fluids by granitic rocks (Heinrich, 1990; Lecumberri-Sanchez et al., 2017; Liu et al., 2014, 2015; Polya, 1988).

The tungsten species in NaCl aqueous solutions included in the model are $\text{H}_2\text{WO}_4^0$, $\text{HWO}_4^-$, and $\text{WO}_3^2-$ (Redkin, 2010; Wang et al., 2019a; 2019b; Wood and Samson, 2000). Wood and Samson (2000) postulated the existence of alkaline tungstate ion pairs such as $\text{NaHWO}_4^0$ and $\text{NaWO}_3^-$ in their model, but their postulation is supported neither by molecular dynamic simulations conducted by Mei et al. (2019) nor by solubility experiments conducted by Wang et al. (2019b). Therefore, neither $\text{NaHWO}_4^0$ nor $\text{NaWO}_4^-$ are incorporated in the present models.

The valence states of iron (Fe) and manganese (Mn) ions are sensitive to oxygen fugacity. Hydrothermal fluids in the crust generally have a low oxidation potential, and dissolved Fe is predominantly in the +2 oxidation state (Heinrich and Seward, 1990; Testemale et al., 2009). Under the reduced conditions of W-mineralizing fluids, the amount of Fe$^{3+}$ in hydrothermal fluids is negligible compared to that of Fe$^{2+}$ (cf. Wood and Samson, 2000). Mn occurs in the valence states of +2, +3, and +4 in natural environments (Wolfram and Krupp, 1996). However, transport of Mn in hydrothermal fluids is widely accepted to be in the +2 oxidation state (cf. Gammons and Seward, 1996; Tian et al., 2014). Thus, the effect of oxygen fugacity was implicitly considered and Fe$^{2+}$, Mn$^{2+}$, and their reactions with Cl$^-$ and OH$^-$ were incorporated in the models.
The solubility product of FeWO$_4$ was modeled by Wood and Samson (2000) using the thermodynamic data in SUPCRT (Shock et al., 1992) and the temperature-dependent heat capacity of ferberite proposed by Polya (1990). Wood and Samson (2000)’s method was used to reproduce the solubility product of FeWO$_4$. However, the solubility product of MnWO$_4$ and the equilibrium constant of MnCl$_2^0$ formation cannot be calculated using current thermodynamic database (e.g. SUPCRT updated by 2017, see http://geopig.asu.edu/). Empirical formulas were developed to fill this gap. Molality (mol/kg) was used for the concentrations of the species in this study.

### 3.1 The solubility product of MnWO$_4$

The dissolution reaction of MnWO$_4$ in aqueous solutions is as follows:

\[
\text{MnWO}_4(s) \rightleftharpoons \text{Mn}^{2+}(aq) + \text{WO}_4^{2-}(aq) \quad (3)
\]

The solubility product $K_{sp}$ was calculated by the following equation:

\[
\log K_{sp} = \frac{-\Delta_r G^0_{PT}}{\log(10)RT} \quad (4)
\]

in which $\log$ is the common logarithm, $R$ is the universal gas constant (8.31446 J K$^{-1}$mol$^{-1}$), and $T$ is the temperature in K. The standard reaction Gibbs energy $\Delta_r G^0_{PT}$ for the reaction (1) is:

\[
\Delta_r G^0_{PT} = \Delta_f G^0_{PT}(\text{Mn}^{2+}) + \Delta_f G^0_{PT}(\text{WO}_4^{2-}) - \Delta_f G^0_{PT}(\text{MnWO}_4) \quad (5)
\]

The $\Delta_f G^0_{PT}$ of a solid species (e.g. MnWO$_4$ and FeWO$_4$) is a function of $T$, $P$ as follows:

\[
\Delta_f G^0_{PT} = \Delta_f G^0_{298.15K,1bar} - S^0_{298.15}(T - 298.15) + \int_{298.15}^{T} C^0_P dT - T \int_{298.15}^{T} \frac{C^0_P}{T} dT + V^0_{298}(P - 1) \quad (6)
\]

where $\Delta_f G^0_{298.15K,1bar}$ is the standard molar Gibbs energy at 298.15 K and 1 bar; $S^0_{298}$ is the standard molar entropy; $C^0_P$ is the isobaric heat capacity; $V^0_{298}$ is the molar volume; $P$ is the
pressure in bar. Except the heat capacity of \( \text{MnWO}_4 \), all the other thermodynamic parameters of \( \text{WO}_4^{2-} \), \( \text{Mn}^{2+} \), and \( \text{MnWO}_4 \) can be accessed from the package SUPCRT (Johnson et al., 1992) and the data compiled by Robie and Hemingway (1995).

Yakovleva and Rezukhina (1960) fitted a heat capacity function of \( \text{MnWO}_4 \) from their experimental data at the temperature range of 293-1074 K (see Fig. 3). However, there is a large gap between their function and the heat capacity of \( \text{MnWO}_4 \) at lower temperatures obtained by Landee and Westrum (1976). To fill this gap, the experimental data of Yakovleva and Rezukhina (1960) and Landee and Westrum (1976) were used to fit the Hass-Fisher heat capacity function against temperature (Haas and Fisher, 1976):

\[
C^0 = A_0 + A_1 T + A_2 T^2 + A_3 T^{-0.5} + A_4 T^{-2} \tag{7}
\]

The fitted coefficients \( A_0 - A_4 \) are shown in Table 1, and Supplementary data 1 lists the experimental data used for fitting. Compared to the function of Yakovleva and Rezukhina (1960), the heat capacity function fitted here joins smoothly with the low-temperature data, and \( C^0 \) asymptotically approaches a limit at high temperature as required by theory (cf. Kieffer, 1985). The heat capacity of \( \text{MnWO}_4 \) from 298 to 900 K is 3-6% lower than that of \( \text{FeWO}_4 \) (Fig. 4a).

The \( \Delta_f G^0_{PT} \) of \( \text{MnWO}_4 \) was derived by substituting the fitted heat capacity function and other thermodynamic data of \( \text{MnWO}_4 \) in Table 1 into the equation (6) (see Supplementary data 2). The \( \Delta_f G^0_{PT} \) of \( \text{MnWO}_4 \) from 200 to 400 °C is 8-9% higher than that of \( \text{FeWO}_4 \) (Fig. 4b). The \( \Delta_f G^0_{PT} \) of \( \text{Mn}^{2+} \), \( \text{Fe}^{2+} \), and \( \text{WO}_4^{2-} \) were calculated from the thermodynamic data in SUPCRT (see Fig. 5). Thus, the solubility product \( K_{sp} \) of \( \text{MnWO}_4 \) was reproduced by the equation (4). Horner (1979) also reproduced the \( K_{sp} \) of \( \text{MnWO}_4 \) using the empirical formula proposed by Chernysh and Ivanova (1969), but his \( K_{sp} \) differs from that of this study by three orders of magnitude maximum (Fig. 6). \( K_{sp} \) of \( \text{MnWO}_4 \) reproduced by this study...
seems more reasonable because the thermodynamic data required for calculating the standard reaction Gibbs energy of MnWO₄ dissolution differ from those of FeWO₄ within one order of magnitude (Table 1 and Fig. 3-5). Thus, the solubility product of MnWO₄ fitted by this study was used in the model.

### 3.2 The formation constant of MnCl₂⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻˓•  

Mn is transported mainly in the form of Mn²⁺ and chloride complexes like MnCl₂⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻˓•  in hydrothermal fluids (Boctor, 1985; Gammons and Seward, 1996; Suleimenov and Seward, 2000). Several laboratory experiments have been conducted to determine equilibrium constants of Mn²⁺ + 2Cl⁻ = MnCl₂⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻˓•  at high temperatures. Gammons and Seward (1996) measured the formation constants of MnCl₂⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻˓•  at temperatures up to 300 °C using solubility measurements, and Suleimenov and Seward (2000) using ultraviolet spectra. Tian et al. (2014) also measured formation constants of MnCl₂(H₂O)₂ at temperatures up to 550 °C using in situ X-ray absorption spectroscopy. The three sources of experimental data were used to fit the density model of Anderson et al. (1991), respectively:

\[
\ln K = p_1 + p_2/T + p_3\ln \rho/T \quad (8)
\]

, in which \(\ln K\) is the natural logarithm of the equilibrium constant \(K\), \(p_1, p_2, p_3\) are empirical parameters, and \(\rho\) is water density. The IAPWS-95 formulation was used to reproduce water density (Wagner and Pruss, 2002). The three empirical equations have a high fitting degree (Table 2 and Fig. 7a-7c).

The three empirical equations were used to reproduce formation constants of MnCl₂⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻˓•  at the same temperature and pressure conditions (Fig. 7d). The values of Gammons and Seward (1996) and Tian et al., (2014) are higher than those of Suleimenov and Seward
(2000) at 300-400 °C. Both MnCl₂(H₂O)₂ (a tetrahedral complex) and MnCl₂(H₂O)₄ (a octahedral complex) exist in hydrothermal fluids at temperatures over 200 °C, and the former exceeds the latter over 300 °C (Tian et al., 2014). This suggests that formation constants of MnCl⁰ at temperatures over 200 °C should be higher than those of MnCl₂ (H₂O)₂; therefore, the experimental data of Suleimenov and Seward (2000) may underestimate the formation constants of MnCl⁰ at temperatures ≥ 300 °C. The formation constants of MnCl₂(H₂O)₂ fitted from Tian et al., (2014) are 0.44-0.72 log units lower than those of MnCl⁰ fitted from Gammons and Seward (1996). A reasonable explanation for this difference is that the formation constants of MnCl⁰ from Gammons and Seward (1996) probably includes contributions from both the MnCl₂(H₂O)₂ and MnCl₂(H₂O)₄ identified by Tian et al., (2014). Therefore, the empirical equation fitted from Gammons and Seward (1996) was used in the models.

3.3 High-order Fe (II) and Mn (II) chloride complexes

High-order chloride complex of Fe (II) and Mn (II) were found using X-ray absorption spectroscopy measurements (e.g. Testemale et al., 2009; Tian et al., 2014). FeCl⁴⁻, a higher order chloride complex of Fe (II) is stable at high temperature (>300 °C) and high chloride molality (>2 mol/kg) (Testemale et al., 2009). MnCl₃⁻, a higher order chloride complex of Mn (II), was found to be the dominant species in high-salinity (>3 mol/kg chloride) and high-temperature (≥ 400 °C) solutions. The conditions of the dominance of these two high-order chloride complexes overlap the mineralizing conditions of tungsten deposits in the world. Thus, FeCl⁴⁻ and MnCl₃⁻ were considered in the models presented here.
The formation constants of $\text{FeCl}_4^{2−}$ from Testemale et al., (2009) and the formation constants of $\text{MnCl}_3^{−}$ from Tian et al., (2014) were employed to fit the density model (equation 8), respectively. The empirical functions fit those experimental data well (see Table 2), and formation constants of both $\text{FeCl}_4^{2−}$ and $\text{MnCl}_3^{−}$ increase with temperature but decrease with pressure (Fig. 8).

4. Thermodynamic modeling for fluids in the W-Mn-Cl-Na-O-H and W-Fe-Cl-Na-O-H systems

Wolframite solubility in hydrothermal fluids was constraint by thermodynamic models in the W-Mn-Cl-Na-O-H and W-Fe-Cl-Na-O-H systems, respectively. For the W-Mn-Cl-Na-O-H system, $\text{MnWO}_4$ was assumed to be saturated in hydrothermal fluids. Seventeen equations were incorporated in the models to solve the concentrations of the seventeen species (Table 3). Among those equations, thirteen non-linear equations were established from the thirteen reactions. For example, the non-linear equation for the association of $\text{Na}^+$ and $\text{Cl}^−$ into $\text{NaCl}^\circ$ (the fifth reaction in Table 3) is:

$$\log K = \frac{\gamma_{\text{NaCl}^\circ}[\text{NaCl}^\circ]}{\gamma_{\text{Na}^+}[\text{Na}^+][\text{Cl}^−]}$$ (8)

in which $\log K$ is the equilibrium constant; $[\text{NaCl}^\circ]$ and $\gamma_{\text{NaCl}^\circ}$ are the concentration and the activity coefficient of $\text{NaCl}^\circ$ in aqueous solutions. The other four equations were obtained from the charge and mass balance relations shown in Table 3.

Similarly, $\text{FeWO}_4$ was assumed to be saturated in hydrothermal fluids in the thermodynamic model for the W-Fe-Cl-Na-O-H system. Another seventeen equations were established from thirteen reactions and four charge and mass balance relations shown in
The activity of a species in electrolyte solutions is its effective concentration and equals its concentration multiplied by its activity coefficient. The activity coefficients of electrically charged species in the models were calculated by an extended Debye-Hückel equation as parameterized by Helgeson et al. (1981) for NaCl-dominated solutions to high pressure and temperature:

\[ \log \gamma_i = \frac{-Az_i^2 \sqrt{I}}{1 + aB \sqrt{I}} + bI \]  
\[ I = \frac{1}{2} \sum_{i=1}^{n} c_i z_i^2 \]

in which \( \gamma_i \) is the activity coefficient, \( z_i \) is the charge number, \( A \) and \( B \) are two parameters related to the dielectric constant and density of water, \( a \) and \( b \) are temperature-dependent constants, \( I \) is the ionic strength in mol/kg, and \( c_i \) is the molar concentration. The activity coefficients of the neutral species (e.g. HCl, NaCl) and the activity of \( \text{H}_2\text{O} \) in our models were assumed to unity.

Activity coefficients of charged species and the equilibrium constants of the reactions were calculated using the R package CHNOSZ developed by Dick (2019). CHNOSZ is an open-source R language package that uses the revised Helgeson-Kirkham-Flowers electrostatic equations of state (Helgeson et al., 1981) and the thermodynamic properties of minerals and aqueous species in SUPCRT (Johnson et al., 1992). The extended term parameter (‘B-dot’) of the extended Debye-Hückel equation in CHNOSZ is derived from the data of Helgeson (1969) and Helgeson et al., (1981) and explorations of Manning et al. (2013) who predicts values of B-dot up to 1000 °C and 30 kbars using the empirical...
correlations with the density of water. The nonlinear equations were solved using another R language package rootSolve (cf. Soetaert and Herman, 2008), and the solving process is shown in Appendix 1.

The temperature, pressure, salinity, and pH levels used in the models are 300-400 °C, 500-1500 bars, 5-15 wt. % NaCl equivalent, and pH=3-9, respectively (see section 2). The model of $\lambda = 10$ (equations 1 and 2) was first calculated and compared to the results of $\lambda = 100$ and $\lambda = 1000$. The output of all the calculations is listed in Supplementary data 3.

5. Results

5.1 W-Mn-Cl-Na-O-H system

It was assumed that $\lambda = 10$ was fixed in the model. The dominant tungsten species at 300-400 °C changes from $\text{H}_2\text{WO}_4^0$, $\text{HWO}_4^-$, to $\text{WO}_4^{2-}$ as pH increases from 3 to 9 (Fig. 9a and 9c). Manganese species at 400 °C is dominated by $\text{MnCl}_2^0$ independent on pH. The dominant manganese species at 300 °C changes to $\text{MnO}_2^0$ as pH moves to alkaline levels.

A few to thousands of ppm tungsten can be dissolved in hydrothermal fluids. Hübnerite solubility is positively correlated to fluid temperature and salinity (Fig. 10). Note that hübnerite solubility at alkaline conditions is less sensitive to temperature than that at acidic conditions. More tungsten would dissolve as pH moves towards more acidic and more alkaline conditions. Hübnerite solubility decreases with increasing fluid pressure at pH<8.5 (Fig. 11). Typical W-mineralizing fluids with a pH=4-6 can dissolve a few to hundreds of ppm tungsten, while alkaline hydrothermal fluids dissolve tens of ppm at most.

Hübnerite solubility decreases by approximately one order of magnitude as $\lambda$ increases.
from 10 to 1000 (Fig. 12). A few to hundreds ppm of tungsten can be dissolved in hydrothermal fluids with a pH=4-6.

5.2 W-Fe-Cl-Na-O-H system

\( \lambda = 10 \) was first used in the model of W-Fe-Cl-Na-O-H. Iron species is dominated by FeCl\(_2^+\) at pH<7 and by HFeO\(_2^-\) at pH>8 (Fig. 13). The curve of ferberite solubility against pH is an upward-opening parabola. Acidic hydrothermal fluids dissolve approximately 1000 ppm tungsten at most, while alkaline hydrothermal fluids can contain hundreds of ppm tungsten (Fig. 14). Ferberite solubility increases with fluid temperature and salinity at acidic conditions but it becomes insensitive to fluid temperature and salinity at alkaline conditions (Fig. 14). The influence of fluid pressure on ferberite solubility depends on pH (Fig. 15). A few to hundreds of ppm tungsten can be dissolved in hydrothermal fluids with pH=4-6. Fig. 16 shows that an increase of \( \lambda \) from 10 to 1000 causes a decrease of ferberite solubility by 1-1.5 orders of magnitude.

5.3 difference between Mn and Fe molalities at a fixed W concentration

To examine the difference between Mn and Fe in hydrothermal fluids, the concentration of total tungsten species in hydrothermal fluids was fixed to replace the mass constraints expressed by equation (1) and (2) for the models of W-Mn-Cl-Na-O-H and W-Fe-Cl-Na-O-H, respectively. Tungsten concentrations of 50 ppm and 200 ppm were used in the models (see Fig. 1), and other charge and mass constraints remained unchanged. Thus, the molalities of Mn and Fe in the two models were calculated, respectively. In hydrothermal fluids with 50 ppm W, 1.4-5.4 times more Mn is needed than Fe at acidic conditions, while 2-3 orders of magnitude more Fe is needed than Mn at alkaline conditions (Fig. 17). Increasing the fixed
tungsten concentration to 200 ppm does not alter the trend of more Mn in acidic hydrothermal fluids and more Fe at alkaline conditions (Fig. 18).

6. Discussion

6.1 Comparisons to other thermodynamic modeling and experimental results

The thermodynamic predictions in Wood and Samson (1998) show that the predominant tungsten species changes from $\text{H}_2\text{WO}_4^0$ and $\text{HWO}_4^-$ to $\text{WO}_4^{2-}$ as pH increases from acidic to alkaline conditions (see their Fig. 4). This is in accord with the dominant W species shown in Fig. 9a and 9c.

Tian and his co-authors (2014) also calculated the Mn(II) species percentages with HCl concentrations from 0.0003 to 0.0043 mol/kg from 200 to 450 °C. From their Fig. 9, concentrations of $\text{MnCl}_2^0$ (the sum of $\text{MnCl}_2(\text{H}_2\text{O})_2$ and $\text{MnCl}_2(\text{H}_2\text{O})_4$) exceed those of $\text{MnCl}_3^-$ under conditions of 300-400 °C and 10 wt. % NaCl equivalent. This is consistent with the results of this study at acidic conditions (Fig. 9b and 9d).

$\text{FeCl}_2^{2-}$ is the dominant iron(II) species at acidic conditions in the model of W-Fe-Cl-Na-O-H (Fig. 13). This is consistent with the calculations of Testemale et al., (2009). At alkaline conditions, the dominant iron(II) species changes to be $\text{HFeO}_2^-$ (Fig. 13), which is also consistent with the results in Wood and Samson (2000).

Recent crystallization experiments of hübnerite suggest that hübnerite is significantly dissolved in strongly alkaline fluids at 300-400 °C (Li et al., 2018a). This is accord with the high hübnerite solubility in alkaline fluids found from this study (see Fig. 10 and 11).

6.2 Wolframite solubility and precipitation mechanisms

Thermodynamic models in the W-Mn-Cl-Na-O-H and W-Fe-Cl-Na-O-H systems put two
end-member constraints on wolframite solubility and precipitation mechanisms in hydrothermal fluids. Both hübnerite and ferberite solubility in hydrothermal fluids reach a few to hundreds of ppm (Fig. 10, 11, 12, 14, 15, and 16). This is consistent with the W concentrations of fluid inclusions from tungsten deposits in the world (Fig. 1). At pH=4-6, hübnerite solubility is slightly higher than ferberite solubility, while the latter is significantly higher than the former at alkaline conditions (Fig. 10 and 14).

Both hübnerite and ferberite solubilities in hydrothermal fluids decrease as pH moves to neutral levels (Fig. 10 and 14). Therefore, neutralization by fluid mixing or fluid-rock interaction would cause precipitation of hübnerite and ferberite. A decrease in temperature also precipitates hübnerite and ferberite from acidic fluids, but simple cooling becomes less efficient in precipitating ferberite and hübnerite at alkaline conditions (Fig. 10 and 14). This may explain why alkali metasomatism (e.g. albitization) causes little W mineralization in tungsten deposits (e.g. He, 1987; Hu et al., 2004; Liu and Ma, 1993; Pirajno and Schlogl, 1987; Zhang et al., 2018b). A decrease in fluid salinity could also precipitate hübnerite and ferberite from acidic fluids, but ferberite solubility in alkaline fluids is less sensitive to fluid salinity than in acidic fluids. The insensitivity of wolframite solubility to temperature and salinity may prevent precipitation of wolframite from alkaline fluids and allow significant tungsten mineralization at later stages. This may explain why the main mineralization stage of giant tungsten deposits occurred at greisen stages rather than at alkaline stages (e.g. the Dahutang tungsten deposit in Zhang et al., 2018b).

It is found from this study that a decrease in fluid pressure increases solubilities of both hübnerite and ferberite solubility in acidic hydrothermal fluids (Fig. 11 and 15); therefore,
fluid pressure drop cannot cause wolframite precipitation. This is in contrast with Liu et al. (2018) where CO₂ loss accompanying a drop in fluid pressure is found to be effective mechanisms for ferberite precipitation. This gap can be reconciled by that the influence of fluid pressure on wolframite solubility depends on the existence of CO₂ in mineralizing fluids.

6.3 Mn/Fe ratios in wolframite

The thermodynamic models presented here provide an insight into the factors controlling Mn/Fe ratios in wolframite. The availability of Fe and Mn is essentially important to precipitate wolframite from the mineralizing fluids (e.g. Jiang et al., 2018; Lecumberri-Sanchez et al., 2017; Yang et al., 2019; Zhang et al., 2018b). The results of this study suggest that more Mn than Fe is needed to produce mineralizing fluids with the same W concentration at acidic conditions (see the dashed box in Fig. 17 and 18), especially at higher temperatures. This indicates that hübnerite precipitation requires Mn-rich mineralizing fluids, and the Mn/Fe ratio of mineralizing fluids controls the wolframite composition. This is also found by Amossé (1978) using thermo-chemical study of the system MnWO₄-FeWO₄.

At least two factors affect the Mn/Fe ratio of mineralizing fluids. The one factor is the Mn/Fe ratio of the granite magma genetically related to tungsten deposits. Tungsten mineralization is genetically related to the peraluminous S- and I-type granites derived from partial melting of crustal rocks (e.g. Černý et al., 2005; Harlaux et al., 2017; Zhao et al., 2017), which contains more Fe than Mn on average (Rudnick and Gao, 2013). The Fe (II) concentrations in the W-related granites are at least 1-2 orders of magnitude higher than those of Mn (II) (e.g. Bussink, 1984; Hall, 1971; Ramírez and Grundvig, 2000; René, 2018;
Stussi, 1989; Wang et al., 2017). The other factor is the partition coefficients of Mn and Fe between melt and fluid. Zajacz et al. (2008)’s laboratory experiments on coexisting silicate melts and fluid inclusions from the Ehrenfriedersdorf pegmatite in the Erzgebirge suggest that Mn and Fe have similar fluid/melt coefficients. Therefore, W-related magmas tend to release Fe-rich mineralizing fluids rather than Mn-rich ones. This may explain why hübnerite is less common than ferberite in most tungsten deposits. For the case when Mn-rich mineralizing fluids are released from the parental magma or buffered by Mn-rich wallrocks, hübnerite is more likely to precipitate at an early stage. As Mn is consumed, the wolframite precipitated at later stages tends to be relatively Fe-rich. This prediction is consistent with a common phenomenon among vein-type tungsten deposits that wolframite crystallized from early to late shows a decrease in Mn/Fe ratios (Michaud and Pichavant, 2019).

7. Conclusions

Fluid-buffered thermodynamic models of the W-Mn-Cl-Na-O-H and W-Fe-Cl-Na-O-H systems were established to examine chemical controls on wolframite solubility in hydrothermal fluids and Mn/Fe ratios in wolframite. Most thermodynamic data used in the model were accessed from SUPCRT updated until 2017, and the heat capacity of MnWO$_4$, the formation constant of MnCl$_2^0$, MnCl$_5^-$, and FeCl$_4^{2-}$ were fitted from experimental data in the literature. The thermodynamic models provide the following implications:

(1) The predominant tungsten, manganese, and iron species in hydrothermal fluids at typical W-mineralizing conditions are HWO$_4^-$, MnCl$_2^0$ and FeCl$_4^{2-}$, respectively.

(2) Both hübnerite solubility and ferberite solubility in acidic hydrothermal fluids reach up
to hundreds of ppm. Hübnerite and ferberite deposition could be triggered by an increase in pH and a decrease in fluid temperature and salinity. A drop in fluid pressure cannot precipitate hübnerite and ferberite.

(3) Hübnerite and ferberite have a solubility of tens to hundreds of ppm in alkaline hydrothermal fluids, but their solubilities are insensitive to fluid temperature and salinity. This may explain why alkaline metasomatism seldom causes significant W mineralization. The insensitivity of ferberite and hübnerite solubility to fluid temperature and salinity may also prevent W from precipitating from alkaline fluids at an early stage and allow significant W mineralization in later greisens.

(4) The Mn/Fe ratio of mineralizing fluids is the principal variable controlling Mn/Fe ratios in wolframite. More Mn than Fe is needed to maintain hydrothermal fluids with the same W concentration, but more supply of Fe than Mn from the fertile magma tends to produce Fe-rich mineralizing fluids. This may one of reasons why ferberite is more common than hübnerite in tungsten deposits and why hübnerite is more likely to precipitate at an early stage.

Acknowledgements

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used in this study. Tian Yuan’s and Mei Yuan’s explanations also helped X.C. Liu understand different Mn(II) chloride complexes in their paper. The author appreciates Weihua Liu, another anonymous reviewer, and the editor for their comments and advices on the original manuscript.

Appendix 1

Nonlinear equations driven by reaction and balance constraints shown in Table 3 and Table 4 were solved by the R package rootSolve. Good initial values of the variables are a prerequisite for deriving the optimal roots (Crerar, 1975). The procedure of solving the nonlinear equations in the models is as follows:

1. The initial ionic strength $I_0$ is set to be half of the mortality of NaCl in solutions, and the initial activities of both Na$^+$ and Cl$^-$ equal $I_0$.

2. Calculate the activity coefficients of all ionic species using the equation (9) with the initial ionic strength $I_0$. Note that the only species-specific parameter required in equation (9) is the electrical charge, meaning that the activity coefficient of Na$^+$ equals that of H$^+$ and the activity coefficient of Fe$^{2+}$ equals that of WO$_4^{2-}$.

3. Calculate the concentration of H$^+$ using its activity coefficient and a given pH. According to the non-linear equations like equation (8), calculate all other species' initial activities one by one using using the initial activities of H$^+$, Na$^+$, and Cl$^-$. These initial activities of ionic species will be used as initial values for solving the nonlinear equations.

4. Solve the nonlinear equations simultaneously using the R package rootSolve. Then, update the ionic strength and the activity coefficients of ionic species and take the roots as the initial values for the next solving.

5. Repeat step (4) until the absolute error of the ionic strength is less than a threshold. A threshold of 0.01 was used in the models, and 3-5 iterations were often needed before
terminating iterations.

Reference


Li, W.S., Ni, Pei, Pan, J.Y., Wang, G.G., Chen, L.L., Yang, Y.L., Ding, J.Y., 2018b. Fluid inclusion characteristics as an indicator for tungsten mineralization in the Mesozoic Yaogangxian tungsten deposit, central Nanling district,


Zhang, C., 1981. The temporal and spatial characteristics of wolframite composition in the tungsten deposits in Jiangxi.


Zhang, Y., Gao, J.F., Ma, D.S., Pan, J.Y., 2018b. The role of hydrothermal alteration in tungsten mineralization at the Dahutang tungsten deposit, South China. Ore Geol. Rev., 95: 1008-1027.

\[ \text{Mn}^{2+} + 3 \text{Cl}^- = \text{MnCl}_3 \]

\[ \text{Fe}^{2+} + 4 \text{Cl}^- = \text{FeCl}_4^{2-} \]
Table 1 The thermodynamic data of FeWO$_4$ and MnWO$_4$

<table>
<thead>
<tr>
<th></th>
<th>$\Delta f^oG_{298}$ (kJ/mol)</th>
<th>$S^o_{298}$ (JK$^{-1}$mol$^{-1}$)</th>
<th>$C_p$(JK$^{-1}$mol$^{-1}$)</th>
<th>$\vartheta^o_{298,1bar}$ (J bar$^{-1}$mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn, 10 wt% NaCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn, 15 wt% NaCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe, 10 wt% NaCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe, 15 wt% NaCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

34
The $\Delta_f \mu_{298}^0$ and $C_p$ of FeWO$_4$ are from Polya (1990), and the $C_p$ of MnWO$_4$ was fitted in this study. The other parameters are from Robie and Hemingway (1995).

Table 2 the fitted coefficients for the formation constants of MnCl$_2^0$, MnCl$_2$(H$_2$O)$_2$, FeCl$_4^{2-}$, and MnCl$_3^{-}$.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$p_1$</th>
<th>$p_2$ (K)</th>
<th>$p_3$ (K m$^3$/kg)</th>
<th>Data sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$^{2+}$ + 2Cl$^-$ = MnCl$_2^0$</td>
<td>12.82</td>
<td>143203.80</td>
<td>-21707.02</td>
<td>1</td>
</tr>
<tr>
<td>Mn(H$_2$O)$_6^{2+}$ + 2Cl$^-$ = MnCl$_2$(H$_2$O)$_2$(aq) + 4H$_2$O</td>
<td>23.00</td>
<td>38543.20</td>
<td>-6947.83</td>
<td>2</td>
</tr>
<tr>
<td>Mn$^{2+}$ + 2Cl$^-$ = MnCl$_2^0$</td>
<td>17.99</td>
<td>116125.25</td>
<td>-18171.62</td>
<td>3</td>
</tr>
<tr>
<td>Fe$^{2+}$ + 4Cl$^-$ = FeCl$_4^{2-}$</td>
<td>-7.35</td>
<td>-15516.49</td>
<td>23144.03</td>
<td>4</td>
</tr>
<tr>
<td>Mn$^{2+}$ + 3Cl$^-$ = MnCl$_3^{-}$</td>
<td>20.18</td>
<td>106765.42</td>
<td>-16943.63</td>
<td>3</td>
</tr>
</tbody>
</table>

1, Gammons and Seward (1996); 2, Suleimenov and Seward (2000); 3, Tian et al., (2014); 4, Testemale et al., (2009).

Table 3 Chemical reactions and mass and charge balance constraints for the model of W-Mn-Cl-Na-O-H system.

<table>
<thead>
<tr>
<th>Number</th>
<th>Reaction and balance constraints</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H$_2$O = H$^+$ + OH$^-$</td>
</tr>
<tr>
<td>Number</td>
<td>Reaction and balance constraints</td>
</tr>
<tr>
<td>--------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>2</td>
<td>$H^+ + Cl^- = HCl^0$</td>
</tr>
<tr>
<td>3</td>
<td>$H^+ + WO_4^{2-} = HWO_4^-$</td>
</tr>
<tr>
<td>4</td>
<td>$H^+ + HWO_4^- = H_2WO_4^0$</td>
</tr>
<tr>
<td>5</td>
<td>$Na^+ + Cl^- = NaCl^0$</td>
</tr>
<tr>
<td>6</td>
<td>$Na^+ + H_2O = NaOH^0 + H^+$</td>
</tr>
<tr>
<td>7</td>
<td>$MnWO_4(s) = Mn^{2+} + WO_4^{2-}$</td>
</tr>
<tr>
<td>8</td>
<td>$Mn^{2+} + Cl^- = MnCl^+$</td>
</tr>
<tr>
<td>9</td>
<td>$Mn^{2+} + 2Cl^- = MnCl_2^0$</td>
</tr>
<tr>
<td>10</td>
<td>$Mn^{2+} + 3Cl^- = MnCl_3^-$</td>
</tr>
<tr>
<td>11</td>
<td>$Mn^{2+} + H_2O = MnOH^+ + H^+$</td>
</tr>
<tr>
<td>12</td>
<td>$Mn^{2+} + H_2O = MnO^0 + 2H^+$</td>
</tr>
<tr>
<td>13</td>
<td>$Mn^{2+} + 2H_2O = HMnO_2^- + 3H^+$</td>
</tr>
<tr>
<td>14</td>
<td>Charge balance</td>
</tr>
<tr>
<td></td>
<td>$[H^+] + [Na^+] + 2[Mn]^{2+} + [MnCl^+] + [MnOH^+] = [OH^-] + [Cl^-] + [HWO_4^-] + 2[WO_4^{2-}] + [MnCl_2^+] + [HMnO_2^-]$</td>
</tr>
<tr>
<td>15</td>
<td>Cl mass balance</td>
</tr>
<tr>
<td></td>
<td>$\Sigma Cl = [Cl^-] + [HCl^0] + [NaCl^0] + [MnCl^+] + 2[MnCl_2^0] + 3[MnCl_3^0]$</td>
</tr>
<tr>
<td>16</td>
<td>$\Sigma W = \Sigma Mn/\lambda$</td>
</tr>
<tr>
<td></td>
<td>$\lambda ([H_2WO_4^0] + [HWO_4^-] + [WO_4^{2-}]) = [Mn^{2+}] + [MnCl^+] + [MnCl_2^0] + [MnCl_3^0] + [MnOH^+] + [MnO^0] + [HMnO_2^-]$</td>
</tr>
<tr>
<td>17</td>
<td>A given pH from 3 to 9</td>
</tr>
<tr>
<td></td>
<td>$[H^+] = 10^{-pH}/\gamma_H^*$</td>
</tr>
</tbody>
</table>

[ · ] represents the species’ molality in solutions. $\lambda$ is a constant ranging from 10 to $10^3$.  

Table 4 Chemical reactions and mass and charge balance constraints for the model of W-Fe-Cl-Na-O-H system
<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H₂O = H⁺ + OH⁻</td>
</tr>
<tr>
<td>2</td>
<td>H⁺ + Cl⁻ = HCl⁰</td>
</tr>
<tr>
<td>3</td>
<td>H⁺ + WO₄²⁻ = HWO₄⁻</td>
</tr>
<tr>
<td>4</td>
<td>H⁺ + HWO₄⁻ = H₂WO₄⁰</td>
</tr>
<tr>
<td>5</td>
<td>Na⁺ + Cl⁻ = NaCl⁰</td>
</tr>
<tr>
<td>6</td>
<td>Na⁺ + H₂O = NaOH⁰ + H⁺</td>
</tr>
<tr>
<td>7</td>
<td>FeWO₄(s) = Fe²⁺ + WO₄²⁻</td>
</tr>
<tr>
<td>8</td>
<td>Fe²⁺ + Cl⁻ = FeCl⁺</td>
</tr>
<tr>
<td>9</td>
<td>Fe²⁺ + 2Cl⁻ = FeCl₂⁰</td>
</tr>
<tr>
<td>10</td>
<td>Fe²⁺ + 4Cl⁻ = FeCl₄²⁻</td>
</tr>
<tr>
<td>11</td>
<td>Fe²⁺ + H₂O = FeOH⁺ + H⁺</td>
</tr>
<tr>
<td>12</td>
<td>Fe²⁺ + H₂O = FeO⁰ + 2H⁺</td>
</tr>
<tr>
<td>13</td>
<td>Fe²⁺ + 2H₂O = HFeO₂⁻ + 3H⁺</td>
</tr>
</tbody>
</table>

14. Charge balance: 
\[ [\text{H}^+]+[\text{Na}^⁺]+2[\text{Fe}^{2+}]+[\text{FeCl}^+]+[\text{FeOH}^+]= [\text{OH}^-]+[\text{Cl}^-]+[\text{HWO}_4^-]+2[\text{WO}_4^{2-}]+[\text{HFeO}_2^-]+2[\text{FeCl}_4^{2-}] \]

15. Cl mass balance: 
\[ \sum \text{Cl} = [\text{Cl}^-]+[\text{HCl}^0]+[\text{NaCl}^0]+[\text{FeCl}^+]+2[\text{FeCl}_2^0]+4[\text{FeCl}_4^{2-}] \]

16. ΣW = ΣFe/λ 
\[ \lambda ([\text{H}_2\text{WO}_4^0]+[\text{HWO}_4^-]+[\text{WO}_4^{2-}]) = [\text{Fe}^{2+}]+[\text{FeCl}^+]+[\text{FeCl}_2^0]+[\text{FeOH}^+]+[\text{FeO}^0]+[\text{HFeO}_2^-]+[\text{FeCl}_4^{2-}] \]

17. A given pH from 3 to 9 
\[ [\text{H}^+] = 10^{-\text{pH}} / \gamma_{\text{H}} \]

[
\cdot
] represents the species' molality in solutions. λ is a constant ranging from 10 to 10³.

Fig. 1 The heat capacity of MnWO₄ fitted from experimental data of Yakovleva and Rezukhina (1960) and Landee and Westrum (1976)

The squares and dots represent experimental data of Yakovleva and Rezukhina (1960) and Landee and
Westrum (1976), respectively. The red curve is reproduced from the empirical function fitted in this study and the fitting degree $R^2=99.53\%$. The blue curve is reproduced from the function of Yakovleva and Rezukhina (1960).

Fig. 2 Comparisons on the heat capacity (a) and the Gibbs free energy (b) of $\text{FeWO}_4$ and $\text{MnWO}_4$

(a) The heat capacity of $\text{FeWO}_4$ was calculated from the empirical equation proposed by Polya (1990), while the heat capacity of $\text{MnWO}_4$ was reproduced from the empirical equation fitted in this study. (b) The Gibbs free energy of $\text{FeWO}_4$ and $\text{MnWO}_4$ were reproduced by the equation (4) at 1000 bars.

Fig. 3 The Gibbs free energy of $\text{Mn}^{2+}$ and $\text{Fe}^{2+}$ at 1000 bars reproduced from SUPCRT

Fig. 4 The isobaric solubility product of $\text{FeWO}_4$ and $\text{MnWO}_4$

Fig. 5 The formation constants of $\text{MnCl}_2$ fitted from experimental data in the literature

(a) The fitted data are from Gammons and Seward (1996) who conducted solubility experiments at saturated vapour pressures. The fitting degree $R^2=99.99\%$. (b) The experimental data of Suleimenov and Seward (2000) were used. The data were measured at saturated vapour pressures. The fitting degree $R^2=99.87\%$. (c) The formation constants of $\text{MnCl}_2(\text{H}_2\text{O})_2$ in Tian et al., (2014) were used to fit the density model. The fitting degree $R^2=99.98\%$. (d) It compares the formation constants of $\text{MnCl}_2$ at 500 bars reproduced from the three empirical equations.

Fig. 6 The formation constant ($\log K$) of $\text{MnCl}_2^-$ (a) and $\text{FeCl}_4^{2-}$ (b)

(a) The lines are reproduced by fitting the experimental data (the dots) from Testemale et al., (2009). The fitting degree $R^2=99.99\%$. (b) The lines are reproduced by fitting the experimental data (the dots) from Tian et al., (2014). The fitting degree $R^2=99.40\%$.

Fig. 7 Frequency distribution of tungsten concentrations of fluid inclusions in tungsten deposits
The tungsten concentrations (unit in ppm) have been logarithmically transformed with respect to base 10.

Fig. 8 The molality ratios of W/Fe (Fig. 8a, upper), W/Mn (Fig. 8b, lower), and W/(Fe+Mn) (Fig. 8b) of fluid inclusions in tungsten deposits.

Fig. 9 The dominant tungsten (Fig. 9a and 9c) and manganese (Fig. 9b and 9d) species at 500 bars and 10 wt.% NaCl equivalent. The W (Mn) species percentage in Y-axis is calculated by the morlality ratio of a W (Mn) species against the total W (Mn).

Fig. 10 Influences of fluid temperature (a) and salinity (b) on hübnerite solubility. The dashed box represents the typical pH of W-mineralizing fluids.

Fig. 11 Influences of fluid pressure on hübnerite solubility. The dashed box represents the typical pH of W-mineralizing fluids.

Fig. 12 Influences of Mn/W ratios (see $\lambda$ in equation (7)) on hübnerite solubility. The dashed box represents the typical pH of W-mineralizing fluids.

Fig. 13 The dominant iron at 400 °C (a) and 300 °C (b) and 10 wt.% NaCl equivalent. The species percentage in Y-axis is calculated by the morlality ratio of a Fe species against the total Fe.

Fig. 14 Influences of fluid temperature (a) and salinity (b) on ferberite solubility. The dashed box represents the typical pH of W-mineralizing fluids.

Fig. 15 Influences of fluid pressure on ferberite solubility. The dashed box represents the typical pH of W-mineralizing fluids.

Fig. 16 Influences of Fe/W ratios (see $\lambda$ in equation (8)) on ferberite solubility. The dashed box represents the typical pH of W-mineralizing fluids.
Fig. 17 The Mn/Fe molality ratios at a fixed 50 ppm (a) and 200 ppm (b) W concentration

For the case of W=50 ppm, the molalities of Mn and Fe were calculated from the models of W-Mn-Cl-Na-O-H and W-Fe-Cl-Na-O-H, respectively. The dashed box represents the typical pH of W-mineralizing fluids. More Mn than Fe is needed to form mineralizing fluids with the same W concentration.

1. Fluid-buffered thermodynamic models were built for vein-type tungsten deposits.
2. Tungsten solubility in acidic fluids is sensitive to temperature, pH, and salinity.
3. MnWO$_4$ and FeWO$_4$ can be significantly dissolved in alkaline hydrothermal fluids.
4. Tungsten solubility in alkaline fluids is insensitive to temperature and salinity.
5. The Mn/Fe ratio of mineralizing fluids controls Mn/Fe ratios in wolframite.