

黑钨矿有效沉淀机制: CO₂ 逃逸

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摘 要: 黑钨矿是石英脉钨矿床的主要矿石矿物, 其沉淀机制一直存在争议。CO₂ 逃逸能否造成黑钨矿有效沉淀尚缺乏定量模型的评价。文章建立了 W-Fe-Cl-Na-O-C-H 体系的反应平衡模型, 涉及 22 种组分和 16 个化学反应; 相关热力学参数来自 SUPCRT 数据库。模型计算结果表明, pH 与流体压力呈负相关关系, 而钨溶解度与流体压力呈正相关关系; 当成矿流体压力从静岩压力降至静水压力水平, 钨溶解度降幅可达到 27%~47%, 降幅与温度和深度成正比。因而, 降压造成的 CO₂ 逃逸是黑钨矿沉淀的有效机制之一。

关键词: 黑钨矿; 沉淀机制; CO₂ 逃逸; 平衡反应模型

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THE EFFICIENT MECHANISMS FOR PRECIPITATING WOLFRAMITE: CO₂ ESCAPING

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Abstract: Wolframite is the main ore mineral of vein-type tungsten deposits. How wolframite precipitates from hydrothermal fluids is highly disputed in the literature. Whether CO₂ escaping causes significant precipitation of wolframite has not been quantitatively examined. A reaction equilibrium model for the system of W-Fe-Na-Cl-H-C-O was established in this contribution. The model contains 22 species and 16 reactions, the thermodynamic data of which are from the database SUPCRT. The modeling results indicate that pH is negatively correlated to fluid pressure and tungsten solubility is positively correlated to fluid pressure. A decrease in fluid pressure from lithostatic to hydrostatic level could cause a drop of tungsten solubility by 27%~47%, and the decrease degree has a positive correlation to temperature and depth. Therefore, CO₂ escaping accompanying a drop of fluid pressure is one of the mechanisms precipitating wolframite efficiently.

Key words: wolframite; precipitation mechanism; CO₂ escaping; equilibrium reaction modeling

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钨矿是一种岩浆热液型矿床,主要的矿石矿物有白钨矿和黑钨矿^[1-2]。其中,黑钨矿主要赋存在石英脉型黑钨矿床,其沉淀机制存在争议^[3-5]。柳志青^[3]根据黑钨矿在石英脉中的分布规律,提出矿物微粒浓差运离分带的假说,定性地解释黑钨矿集合体(钨砂包)的生长机制。有学者提出钨成矿流体为富硅的岩浆热液过渡性流体,而非简单的水溶液^[4,6-7]。一些学者利用流体包裹体、稳定同位素、高温高压实验和计算模拟等方法提出黑钨矿可能有四种沉淀方式:①简单降温^[8-9];②岩浆水与大气降水混合^[10];③水岩反应^[11];④流体不混溶^[12-14]。其中,流体不混溶的证据主要来自含 CO₂ 的流体包裹体,这种包裹体在南岭地区锡田^[15]、盘古山^[16]、大吉山^[17]、茅坪^[18]等多个石英脉型钨矿中发现。Liu^[19]利用计算模拟发现,水力破裂后热液中 CO₂ 的溶解度可下降 36%。然而,降压后 CO₂ 逃逸如何改变热液化学平衡和钨溶解度有待定量模型的进一步评价。文章通过 NaCl-H₂O-CO₂ 体系反应平衡模型定量分析 CO₂ 逃逸对钨溶解度的影响,以探讨其是否为黑钨矿有效沉淀机制。

1 研究背景

石英脉型黑钨矿床是重要的钨矿床类型之一,主要分布于江西、湖南、广东、广西等地^[2,4,6]。含黑钨矿的石英脉近垂直分布在碱长花岗岩顶部接触带附近^[20],延伸约 1 km^[21-23]。矿石矿物和脉石矿物的流体包裹体研究结果表明钨成矿流体是 NaCl-H₂O±CO₂ 体系,成矿温度一般在 300 ℃~400 ℃,压力可达 90~200 MPa,盐度通常不超过 10wt% NaCl,相关实验数据来自大吉山^[8,17]、瑶岗仙^[9,24,25]、锡田^[11]、盘古山^[16,26]、茅坪^[18]、淘锡坑^[27,28]、漂塘^[29,30]、黄沙^[31]、西华山^[32,33]等石英脉型钨矿床。该类型矿床的产出深度约 4~8 km^[5,32,34]。

目前已在黑钨矿、黄玉、石英等矿石和脉石矿物中发现含 CO₂ 的包裹体,相关研究表明 CO₂ 逃逸触发的流体不混溶是黑钨矿沉淀的重要机制^[18,35-36]。CO₂ 是热液中一种较为常见的挥发份^[37-39],也是热液酸碱平衡的缓冲剂^[40]。压力降低会使热液中 CO₂ 逃逸,引起 pH 升高,从而可能造成矿物质沉淀^[13,40]。故有必要定量地评价 CO₂

逃逸对黑钨矿溶解度的影响。

2 反应平衡模型

地球化学反应平衡模型是以平衡热力学和反应动力学为理论基础,利用数值计算方法,求解相应的非线性方程组,得出研究体系中化学组分的存在形式、浓度和活性等有关信息^[41]。该方法已在斑岩型铜矿^[42-44]、不整合型铀矿^[45-46]、热液型金矿^[47]等多种类型矿床的成矿作用动力学机制研究中发挥重要作用。有学者曾利用含钨体系的反应平衡模型定量分析在钨溶解度与温度、压力、盐度和 pH 的关系,其中 Heinrich^[48]研究了锡钨在盐水体系的溶解度模型,Gibert 等^[49]和龚庆杰等^[50]的平衡反应模型主要针对白钨矿,而 Wood 和 Sammon^[51]关于黑钨矿和白钨矿的溶解度模型最为全面;然而,以往的模型都未考虑 CO₂ 在水溶液的离解反应。文章通过建立 W-Fe-Cl-Na-O-C-H 体系的反应平衡模型,定量分析 CO₂ 逃逸对钨溶解度的影响。

反应平衡模型考虑了 H⁺、OH⁻、HCl⁰、Cl⁻、Na⁺、NaCl⁰、NaOH⁰、H₂WO₄⁰、HWO₄⁻、WO₄²⁻、NaWO₄⁻、NaHWO₄⁰、Fe²⁺、FeCl⁺、FeCl₂⁰、FeOH⁺、FeO⁰、HFeO₂⁻、FeWO₄(s)、CO₂(aq)、HCO₃⁻和 CO₃²⁻共 22 种组分,涉及 16 个化学反应(表 1)及 4 个电荷和质量守恒方程(表 2)。FeWO₄(s) 离解常数、NaWO₄⁻和 NaHWO₄⁰的缔合常数根据 Wood 和 Samson^[51]提出经验公式计算,其余 13 个化学反应的平衡常数根据 SUPCRT 数据库的热力学参数计算^[52]。CO₂ 溶解度根据毛世德^[53]提出的公式计算。有电荷组分的活度系数根据扩展 Deby-Hückel 方程计算^[54];CO₂ 的活度系数根据 Drummond 提出的经验方程计算^[55],其余电中性组分的活度系数为 1。上述平衡常数计算和非线性方程组求解在开源程序 R 下完成。模型所用参数分别为:温度 300~400 ℃,压力 40~200 MPa、盐度 10wt% NaCl,静水压力梯度 10 MPa/km,静岩压力梯度 25 MPa/km,深度 4~8 km。利用 R 语言程序包 CHNOSZ 计算表 1 中的反应平衡常数和有电荷组分的活度系数。FeWO₄(s) 和 CO₂(aq) 不必求解,故有 20 个变量,上述 20 个非线性方程求解利用 R 语言程序包 rootSolve 完成。

表 1 平衡反应模型中的 16 个化学反应

Table 1 The 16 reactions used in the thermodynamic model of this study

序号	化学反应
1	$\text{H}^+ + \text{WO}_4^{2-} = \text{HWO}_4^-$
2	$\text{H}^+ + \text{HWO}_4^- = \text{H}_2\text{WO}_4^0$
3	$\text{H}^+ + \text{Cl}^- = \text{HCl}^0$
4	$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$
5	$\text{FeWO}_4(\text{s}) = \text{Fe}^{2+} + \text{WO}_4^{2-}$
6	$\text{Fe}^{2+} + \text{Cl}^- = \text{FeCl}^+$
7	$\text{Fe}^{2+} + 2\text{Cl}^- = \text{FeCl}_2^0$
8	$\text{Fe}^{2+} + \text{H}_2\text{O} = \text{FeOH}^+ + \text{H}^+$
9	$\text{Fe}^{2+} + \text{H}_2\text{O} = \text{FeO}^0 + 2\text{H}^+$
10	$\text{Fe}^{2+} + 2\text{H}_2\text{O} = \text{HFeO}_2^- + 3\text{H}^+$
11	$\text{Na}^+ + \text{Cl}^- = \text{NaCl}^0$
12	$\text{Na}^+ + \text{H}_2\text{O} = \text{NaOH}^0 + \text{H}^+$
13	$\text{Na}^+ + \text{WO}_4^{2-} = \text{NaWO}_4^-$
14	$\text{Na}^+ + \text{HWO}_4^- = \text{NaHWO}_4^0$
15	$\text{CO}_2(\text{aq}) + \text{H}_2\text{O} = \text{HCO}_3^- + \text{H}^+$
16	$\text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+$

表 2 平衡反应模型中所用的电荷和质量平衡方程

Table 2 Mass and charge balance constraints used in the thermodynamic model

序号	名称	电荷和质量平衡方程
17	电荷平衡方程	$[\text{H}^+] + [\text{Na}^+] + [\text{FeCl}^+] + 2[\text{Fe}^{2+}] + [\text{FeOH}^+] = [\text{HWO}_4^-] + 2[\text{WO}_4^{2-}] + [\text{Cl}^-] + [\text{OH}^-] + [\text{HFeO}_2^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$
18	氯质量平衡方程	$\Sigma\text{Cl} = [\text{Cl}^-] + [\text{HCl}^0] + [\text{NaCl}^0] + [\text{FeCl}^+] + 2[\text{FeCl}_2^0]$
19	$\Sigma\text{Fe} = \Sigma\text{W}$	$[\text{H}_2\text{WO}_4^0] + [\text{HWO}_4^-] + [\text{WO}_4^{2-}] = [\text{FeCl}^+] + [\text{FeCl}_2^0] + [\text{Fe}^{2+}] + [\text{FeOH}^+] + [\text{FeO}^0] + [\text{HFeO}_2^-]$
20	CO ₂ 含量固定	在给定的温度、压力和盐度条件下, CO ₂ 含量达到溶解度 (根据文献 [53] 公式计算)

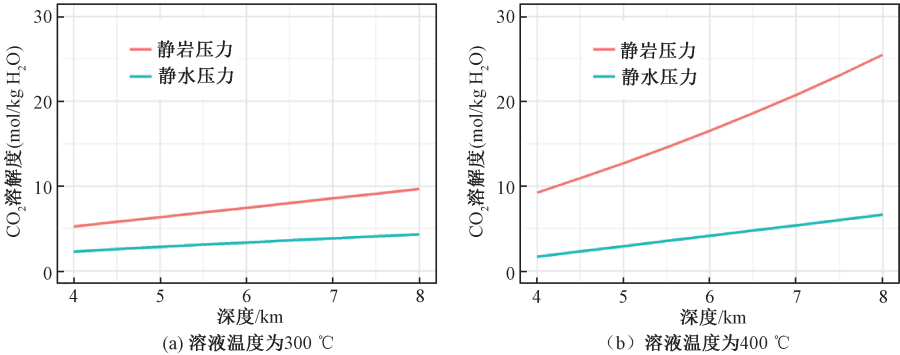


图 1 在 4~8 km 深度的静岩压力和静水压力下 CO₂ 溶解度等温变化曲线

Fig. 1 The isothermal change of CO₂ solubility under the lithostatic and hydrostatic levels at a depth of 4~8 km

压力降至静水压力水平, 热液 pH 上升 0.9~1.2。

(3) 钨溶解度与压力呈正相关关系 (图 3)。当热液温度达到 300 °C, 钨溶解度 $8.19 \times 10^{-6} \sim 18.05 \times 10^{-6}$; 压力从静岩压力降至静水压力水平后, 钨溶解度下降 $3.08 \times 10^{-6} \sim 7.88 \times 10^{-6}$, 降幅 27.3%~43.7%, 平均降幅 36.0%。400 °C 的热液钨溶解度 $59.97 \times 10^{-6} \sim 155.41 \times 10^{-6}$; 流体压力从静岩压力降至静水压力水平后, 钨溶解度下降 $33.80 \times 10^{-6} \sim 72.50 \times 10^{-6}$, 降幅 36%~47%, 平均降幅 41%。降幅比例与深度成正比。

(4) 由图 4 可知, 含钨组分以 HWO_4^- 为主, 其次为 NaWO_4^- 、 NaHWO_4^0 、 H_2WO_4^0 和 WO_4^{2-} 。压力从静岩压力降至静水压力水平后, HWO_4^- 的浓度显著下降。

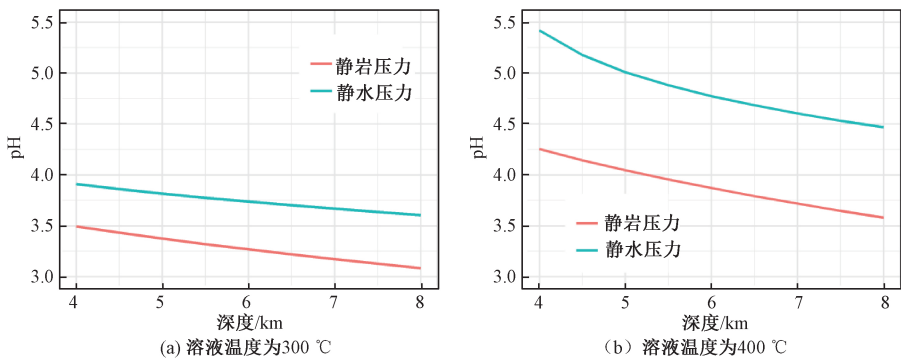


图 2 在 4~8 km 深度的静岩压力和静水压力下 pH 等温变化曲线

Fig. 2 The isothermal change of pH under the lithostatic and hydrostatic levels at a depth of 4~8 km

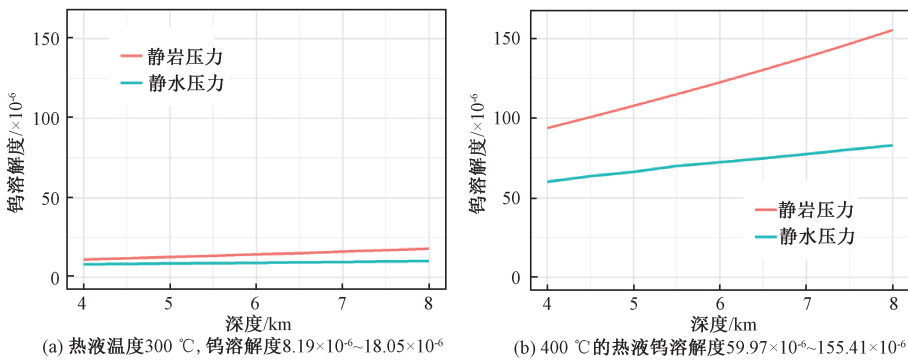


图 3 在 4~8 km 深度的静岩压力和静水压力下钨溶解度等温变化曲线

Fig. 3 The isothermal change of tungsten solubility under the lithostatic and hydrostatic levels at a depth of 4~8 km

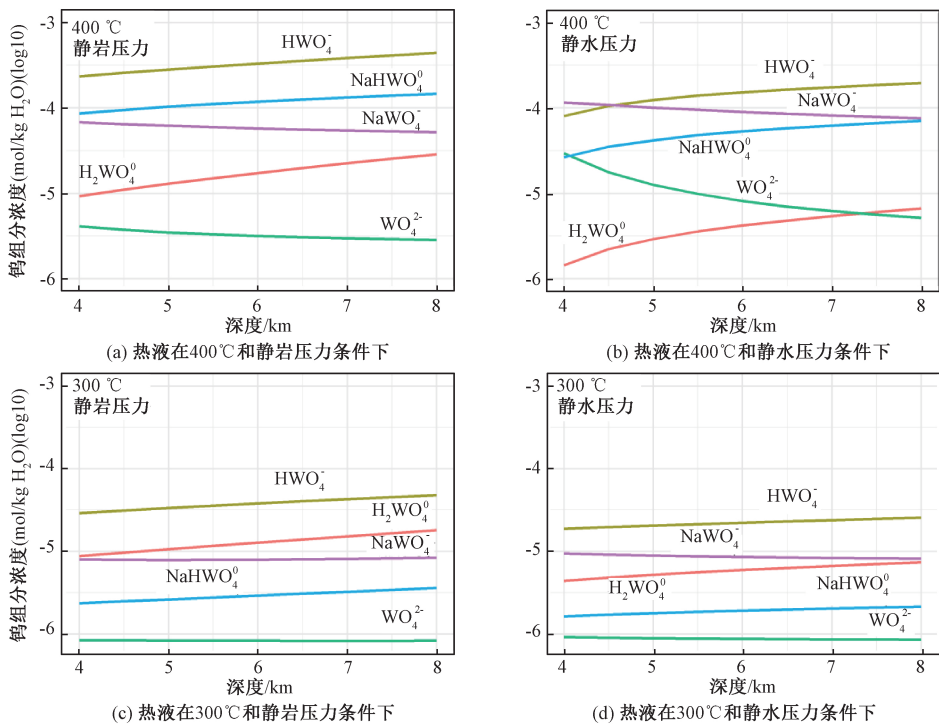


图 4 在 4~8 km 深度的静岩压力和静水压力下含钨组分等温变化曲线

Fig. 4 The isothermal change of tungsten species under the lithostatic and hydrostatic levels at a depth of 4~8 km

4 讨论与结论

目前估算南岭石英脉型黑钨矿成矿流体 pH 的研究极少，少量国外报道的 pH 约为 4~6^[51]。这与模型中 400 ℃ 的热液 pH 范围接近，但高于 300 ℃ 的热液 pH。已发表的数据表明大吉山钨矿和盘古山钨矿成矿流体的 CO₂ 含量已接近饱和状态^[16~17]，因而模型计算的 pH 可作为实际值的下限值；相应地，模型中钨溶解度降幅可作为实际值的上限值。

模型所得出的 pH 范围处于弱酸性环境。在这种环境下，Wood 和 Sammon 得出的含钨组分以 HWO₄⁻ 和 NaWO₄⁻ 为主^[51]。这与模型计算结果一致。

反应平衡模型计算结果表明，在 4~8 km 的成矿深度下，降压造成的 CO₂ 逃逸可使钨溶解度下降 27%~47%；成矿流体温度越高，成矿深度越大，钨溶解度降幅比例越大。位于葡萄牙的 Panasqueira 矿床是世界上最大的锡钨脉型矿床之一，该矿床钨沉淀的效率只有 33%，剩余 67% 被分散在矿体周边钨品位较低的围岩中^[56]。对比可知，单纯的降压可显著降低钨在富含 CO₂ 热液中的溶解度，因而是黑钨矿沉淀的有效机制。

致谢：文章模型计算使用了毛世德教授提供的 CO₂ 溶解度计算程序和两个开源 R 语言程序包：Jeffrey Dick 开发的 CHNOSZ 和 Soetaert 开发的 rootSolve，在此一并表示感谢。

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