

## Research Advances

## Hydraulic Fracturing Leads to Wolframite Deposition at Magmatic-hydrothermal transition

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### Objective

The Nanling Range in southern China is a world-class tungsten province. It is disputed how wolframite as the main ore mineral in the tungsten deposits in this area is precipitated. Wolframite solubility is only weakly dependent on pressure (Wood and Samson, 2000). Therefore, a pressure change cannot alter wolframite solubility. However, fluid inclusions record high-pressure fluids that trigger the initiation and propagation of vein-bearing fractures in these deposits. It is enigmatic whether a decrease in fluid pressure after hydraulic fracturing causes wolframite precipitation from hydrothermal solutions. We first demonstrate that fluid pressure drop after hydraulic fracturing could cause a significant decrease in CO<sub>2</sub> solubility, increase pH, and facilitate wolframite precipitation at magmatic-hydrothermal transition using finite element-based numerical experiments.

### Methods

Finite element-based numerical experiments were conducted to quantify the influence of a hydraulic fracturing process on CO<sub>2</sub> solubility. The coupling of rock deformation and fluid flow was governed by poroelastic constitutive equations, continuity equation, and Darcy's law. These simultaneous partial differential equations were solved by PANDAS. A solubility model was used to calculate CO<sub>2</sub> solubility in aqueous NaCl solutions (Mao et al., 2013). A 2-D numerical model at a depth of 4 km was build based on the structural and geochemical characteristics of tungsten deposits in the Nanling Range. The model has a size of 100 m × 100 m (Fig. 1a). The X axis represents the orientation normal to veins and the Y

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axis is vertical. A background temperature of 400°C was set in the model. The rock had a porosity of 0.5% and a permeability of 10<sup>-17</sup> m<sup>2</sup>. The mechanical parameters of the rock were as follows: Young's modulus 80 GPa, Poisson ratio 0.25, friction angle 30°, cohesion 60 MPa, and tensile strength 5 MPa. The aqueous NaCl solutions had a density of 875 kg/m<sup>3</sup>, a viscosity of 1.18 × 10<sup>-4</sup> Pa·s (Klyukin et al., 2017), and a compressibility of 5.3 × 10<sup>-10</sup> Pa·s.

### Results

A reference point was selected to show the evolution of stresses and fluid flow during the deformation processes. The reference point is 0.02 m above the points with a fixed pressure of 200 MPa. The minimum principle stress at the reference point reached the tensile strength after 6.0 s (Fig. 1b). The fluid pressure at the reference point showed significant fluctuations after yield and decreased from 168 to 119 MPa (Fig. 1c). The decrease in fluid pressure also reduced the CO<sub>2</sub> solubility in aqueous NaCl solutions from 16.6 to 10.4 mol/kg (Fig. 1d).

### Conclusions

Finite element-based numerical experiments are conducted to examine the impact of a hydraulic fracturing process on fluid flow and CO<sub>2</sub> solubility in aqueous NaCl solutions at magmatic-hydrothermal transition. Significant fluctuations of fluid pressure are identified once rock is fractured by high-pressure fluids. The fluid pressure drop after hydraulic fracturing could cause a decrease in CO<sub>2</sub> solubility by 37.3% and increases pH. Because an increase in pH would cause a major decrease in solubility of tungsten (Wood and Samson, 2000), the fluid pressure drop accompanying a hydraulic fracturing process

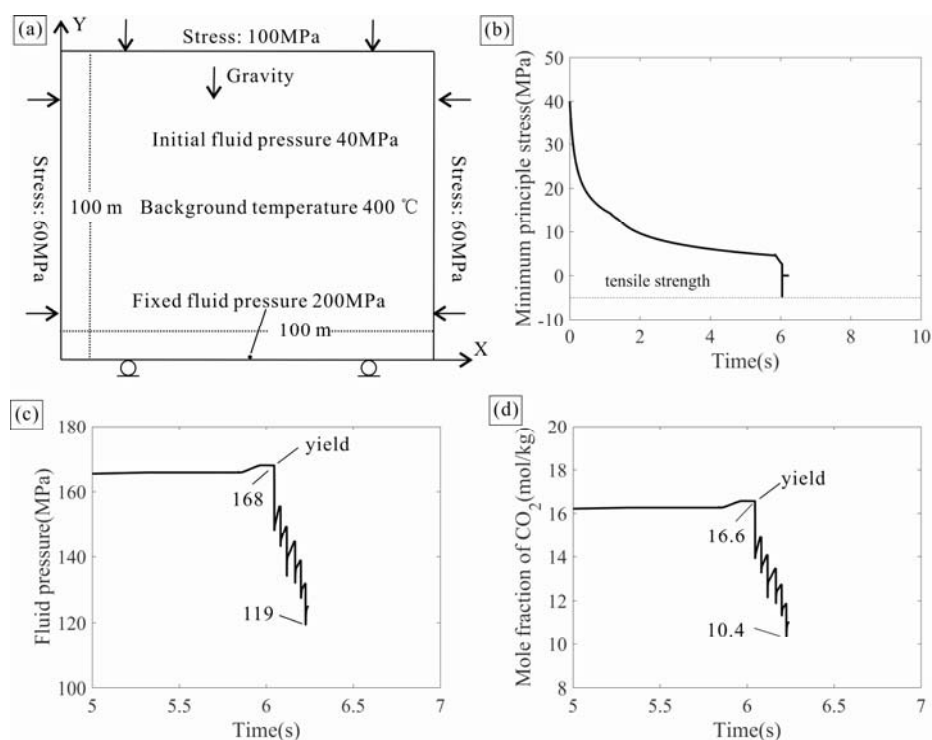


Fig. 1. The numerical model of hydraulic fracturing and the results of the numerical experiments. (a), A 2-D numerical model of hydraulic fracturing; (b), the evolution of the minimum principle stress at the reference point. The reference point is 0.02 m above the points with a fixed pressure of 200 MPa. The compressive stresses are negative and the tensile stress are positive in the model; (c), the evolution of the fluid pressure at the reference point; (d), the evolution of  $\text{CO}_2$  solubility at the reference point.

facilitates wolframite precipitation. Although wolframite solubility is insensitive to pressure (Wood and Samson, 2000), a fluid pressure change during the coupling between rock deformation and fluid flow could alter the solubility of pH-dependent volatiles like  $\text{CO}_2$  and control the wolframite solubility. Therefore, our numerical experiments provide insight into the mechanisms precipitating wolframite at magmatic-hydrothermal transition as well as other metals whose solubility is strongly dependent on pH.

## Acknowledgments

The work is financially supported by the grants from the National Natural Science Foundation of China (41602088, 41373048), Australia Research Council (ARC DP150103467), and the MLR Nonprofit Industry Research Project (201411024). We would like to thank

Mao Shide for providing the code of  $\text{CO}_2$  solubility. Bodnar R.J. and Klyukin Yu.I. are appreciated for providing the viscosity of aqueous NaCl solutions at magmatic-hydrothermal transition.

## References

- Klyukin, Y.I., Lowell, R.P., and Bodnar, R.J., 2017. A revised empirical model to calculate the dynamic viscosity of  $\text{H}_2\text{O}$ -NaCl fluids at elevated temperatures and pressures ( $\leq 1000$  °C,  $\leq 500$  MPa, 0–100wt% NaCl). *Fluid Phase Equilibria*, 433 (Supplement C): 193–205.
- Mao, S., Zhang, D., Li, Y., and Liu, N., 2013. An improved model for calculating  $\text{CO}_2$  solubility in aqueous NaCl solutions and the application to  $\text{CO}_2$ - $\text{H}_2\text{O}$ -NaCl fluid inclusions. *Chemical Geol.*, 347: 43–58.
- Wood, S.A., and Samson, I.M., 2000. The hydrothermal geochemistry of Tungsten in Granitoid environments: I. relative solubilities of ferberite and scheelite as a function of T, P, pH, and Mnacl. *Economic Geol.*, 95: 143–182.