Scheelite U-Pb geochronology and trace element geochemistry fingerprint W mineralization in the giant Zhuxi W deposit, South China

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ABSTRACT

Skarn-type tungsten deposits are widely distributed all over the world and contribute more than 70% of the world’s W supply. The temporal relation between the W mineralization and causative intrusions and the evolution of ore-forming fluids are matters of ongoing debate. In this study, we combine in situ LA-ICP-MS U-Pb dating and trace element compositions of scheelite from Zhuxi, the world’s largest W deposit, and compare them with literature data to address the above issues. Three primary ore stages exist at Zhuxi: prograde skarn, retrograde skarn, and quartz-sulfide stages. Most scheelite occurs in the retrograde skarn stage and is further subdivided into three generations: Sch A, B, and C. The obtained LA-ICP-MS U-Pb ages for three scheelite generations in the Zhuxi deposit are 154.0 ± 2.8, 150.3 ± 3.5, and 150.4 ± 6.3 Ma, respectively, indicating that the entire W mineralization is closely related to the emplacement of the nearby Late Jurassic granites (~154 to 150 Ma, zircon U-Pb ages). In situ LA-ICP-MS trace element results demonstrate that Sch A shows the highest Mo content (mean = 1002 ppm), where those for Sch B and Sch C are 109 and 45 ppm, respectively. These, combined with the gradually increasing trend of Ce contents and δCe values, indicate a shift from oxidizing to reducing conditions for the ore-forming fluid. All three scheelite generations yield significant positive δEu anomalies, which are considered to be unrelated to the redox state, but caused by the addition of Eu (e.g., feldspar dissolution). The high-Y/Ho ratio of scheelite and a good correlation between Y/Ho ratio and δEu (R² = 0.96) suggest that intense fluid-rock interactions between ore fluids and the Shuangqiaoshan Group metasedimentary rocks as well as earlier-formed skarns drove fluid evolution. This study demonstrates that scheelite U-Pb geochronology is a useful technique when identifying the temporal link between hydrothermal W mineralization and the causative intrusion. Our results also highlight that the reactions of the ore fluids with wall rocks and earlier-formed skarns significantly modify the primary fluid compositions.

Keywords: Scheelite LA-ICP-MS U-Pb dating, trace element, skarn W mineralization, Zhuxi, South China

INTRODUCTION

Skarn deposits are one of the most abundant ore deposit types in the Earth’s crust and have been the subject of numerous studies since their discovery (Kwak 1987; Meinert et al. 2005; Romer et al. 2005; Chang et al. 2019). Metal sources for skarn mineralization are critical for establishing robust genetic models for these ore deposits. The close spatial relationship between skarn deposits and plutons indicates a magmatic origin for metals (Audétat et al. 2000; Webster et al. 2004; Thomas et al. 2005; Song et al. 2019). In contrast, some others suggest that the metals originated from the surrounding rocks (Linnen and Williams-Jones 1995; Sun et al. 2019).

To address this issue, scheelite, which is dominant in skarn-type W deposits (Meinert et al. 2005; Song et al. 2014; Sun et al. 2019), can be adopted as an ideal mineral to constrain the compositions and sources of the fluids and the origins of the metals (Song et al. 2014; Poulin et al. 2018; Choi et al. 2020; Han et al. 2020; Su et al. 2021). Scheelite (CaWO₄) commonly accommodates significant amounts of rare earth elements (REE), Y, Mo, and Sr in substitution for Ca or W (Nassau and Loiacono 1963; Ghaderi et al. 1999), which provide insights into the ore-forming processes, including the origin and physicochemical conditions of the ore-forming fluids (Brugger et al. 2002; Song et al. 2014; Hazarika et al. 2016; Cao et al. 2021). Meanwhile, developments in U-Pb geochronology permit direct dating of the ore minerals (e.g., scheelite, cassiterite, and wolframite), thus constraining the timing of the mineralizing events (Yuan et al. 2008; Wintzer et al. 2016; Harlaux et al. 2018). Hence, the combination of geochronology and trace element geochemistry of scheelite will shed new light on understanding the genetic relationship between the W mineralization and the causative intrusions. Here, we present in situ laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) U-Pb ages and