Scheelite composition fingerprints pulsed flow of magmatic fluid in the Fujiashan W skarn deposit, eastern China

YUNHAO JI\textsuperscript{1,2}, GUIQING XIE\textsuperscript{1,2,*}, ROLF L. ROMER\textsuperscript{3}, WEI LI\textsuperscript{1,2}, QIAOQIAO ZHU\textsuperscript{4}, AND BIN FU\textsuperscript{5}

\textsuperscript{1}School of Earth Sciences and Resources, China University of Geosciences, Beijing 100083, China
\textsuperscript{2}MNR Key Laboratory for Exploration Theory & Technology of Critical Mineral Resources, China University of Geosciences, Beijing, 100083, China
\textsuperscript{3}Inorganic and Isotope Geochemistry, GFZ German Research Centre for Geosciences, Telegrafenberg, D-14473 Potsdam, Germany
\textsuperscript{4}MNR Key Laboratory of Metallurgy and Mineral Assessment, Institute of Mineral Resources, CAGS, Beijing 100037, China
\textsuperscript{5}Research School of Earth Sciences, The Australian National University, Canberra, ACT 2601, Australia

\textbf{Abstract}

Scheelite (CaWO\textsubscript{4}) is an economically important W mineral in skarns that form when magmatic fluids exsolved from a granitic intrusion react with carbonate wall rocks. In the Fujiashan W skarn deposit, scheelite formed during four stages of the hydrothermal skarn development. We present cathodoluminescence (CL) images and in situ trace element and Sr-O isotope data of scheelite from these four stages, i.e., scheelite in prograde and retrograde skarn, quartz-sulfide veins, and late calcite replacements. Scheelite from prograde skarn and quartz sulfide veins are homogeneous and show oscillatory zoning textures in CL images, whereas scheelite from retrograde skarn and late carbonate stages display dissolution-reprecipitation and patchy textures. The brightness of CL textures decreases with a higher substitution of Mo. Molybdenum-rich scheelite (up to 2.1 wt\%) is characterized by relatively high contents of Nb and Ta (up to 156 and 0.9 ppm, respectively), positive Eu anomalies, high-\textsuperscript{87}Sr/O values (5.2 to 5.9\%), and relatively low-\textsuperscript{87}Sr/\textsuperscript{86}Sr values (0.70661 to 0.70727), and has grown in a system with a continuous supply of magmatic fluid. Molybdenum-poor scheelite (0.2 wt\%) has low contents of Nb and Ta, negative Eu anomalies, low-\textsuperscript{87}Sr/O values (4.2 to 4.3\%), and relatively high-\textsuperscript{87}Sr/\textsuperscript{86}Sr ratios (0.70748 to 0.70804). This type of scheelite formed in a system with a restricted flow of magmatic fluid during scheelite precipitation became increasingly depleted in elements that substitute into scheelite. The continued reaction of the magmatic fluid with the wall rocks and the precipitation of minerals from the fluid resulted in a systematic change of the \textsuperscript{87}O and \textsuperscript{87}Sr/\textsuperscript{86}Sr ratios. Chemical and isotopic variations in scheelite may reflect the pulsed flow of a magmatic fluid and do not require the involvement of different fluids or contrasting redox conditions.

\textbf{Keywords:} Scheelite, trace element, In-situ Sr-O isotope analysis, pulsed magmatic fluid, skarn

\section*{Introduction}

Skarn deposits are important sources of Sn, W, Cu, Pb, Zn, and high-grade Fe ores (e.g., Chang et al. 2019). Skarns are dominated by calc-silicate minerals such as garnet, pyroxene, and wollastonite and are formed by the interaction of magmatic-hydrothermal fluids emanating from granitic intrusions with carbonate wall rocks (e.g., Meijnt et al. 2005). Commonly, magmatic-hydrothermal fluids migrate along silicate-rich layers and fractures that act as aquifers within the carbonate rocks, whereas the carbonate rock act as aquitards. Consumption of aquifer and aquitard during the formation of skarn minerals increases the permeability, which focuses fluid flow and promotes additional reaction. The reaction-induced increase of permeability is counteracted by the ambient pressure that reduces the interconnectivity of the pores and eventually results in episodic fluid flow (e.g., Cui et al. 2001; Milsch et al. 2003). Reaction-induced changes of the fluid composition induce precipitation of economically relevant elements by the formation of ore minerals, e.g., W in scheelite, or substitution in gangue minerals, e.g., Sn in skarn silicates (e.g., Lefebvre et al. 2019).

Traditionally, the source and evolution of mineralizing fluids in skarn deposits have been studied using O isotope data of bulk gangue mineral separates and hydrogen isotope data of fluid inclusions in gangue minerals (Taylor and O’Neil 1977; Lu et al. 2003). In situ O isotope data of gangue minerals show that the fluid composition may vary during the evolution of the hydrothermal system and mineralization (D’Errico et al. 2012; Ryan-Davis et al. 2019; Li et al. 2022a; Liu et al. 2023). It can be difficult, however, to link variations in the compositions of gangue minerals with the precipitation of ore minerals. Using the compositional variation of ore minerals as a monitor of changing fluid composition and fluid source, as well as changing precipitation conditions, is an approach that removes the uncertainty of the genetic relation between gangue and ore minerals. In W skarn deposits, scheelite seems to be particularly well suited to trace fluid evolution and fluid sources as crosscutting relations and alteration assemblages indicate that scheelite may form during both prograde and retrograde stages (Poulin et al. 2018; Miranda et al. 2022). Due to similar electron configurations...