Nature and timing of Sn mineralization in southern Hunan, South China: Constraints from LA-ICP-MS cassiterite U-Pb geochronology and trace element composition

TAO REN¹, HUAN LI¹*, THOMAS J. ALGEO²,³, MUSA BALA GIREI⁵, JINGHUA WU⁴, AND BIAO LIU¹

¹Key Laboratory of Metallogenic Prediction of Nonferrous Metals and Geological Environment Monitoring, Ministry of Education, School of Geosciences and Info-Physics, Central South University, Changsha 410083, China
²State Key Laboratory of Geological Processes and Mineral Resources, School of Earth Resources, China University of Geosciences, Wuhan 430074, China
³State Key Laboratory of Biogeology and Environmental Geology, School of Earth Sciences, China University of Geosciences, Wuhan 430074, China
⁴Department of Geosciences, University of Cincinnati, Cincinnati, Ohio 42221-0013 U.S.A.
⁵Department of Geology, Bayero University Kano, Kano State, Nigeria

ABSTRACT

Accurately determining the timing and mechanism of metallogenesis of ore deposits is essential for developing a robust genetic model for their exploration. In this paper, we analyze the formation conditions of cassiterite in five major deposits of southern Hunan Province, one of the most important tungsten-tin (W-Sn) provinces in South China, using a combination of cathodoluminescence imaging, in situ U-Pb geochronology, and trace-element concentration data. In situ cassiterite U-Pb geochronology constrains the main period of Sn mineralization to between 155.4 and 142.0 Ma, demonstrating a temporal and genetic relationship to silicic intrusive magmatism in the same area. Three stages of magmatic activity and metallogenic evolution are recognized: (1) Early Paleozoic and Triassic: the initial enrichment stage of tungsten and tin; (2) Jurassic: the metasomatic mineralization stage; and (3) Cretaceous: the magmatic-hydrothermal superposition stage. The cassiterite in these deposits takes four forms, i.e., quartz vein-type, greisen-skarn-type, greisen-type, and granite-type, representing a progression characterized by the increasing content and decreasing range of variation of high field strength elements (HFSEs), and reflecting a general increase in the degree of evolution of the associated granites. Rare earth element (REE) concentrations suggest that precipitation of cassiterite was insensitive to the redox state of the fluid and that precipitation of cassiterite in the southern Hunan Sn deposits did not require a high-fO₂ environment. These findings provide new insights into tin mineralization processes and exploration strategies.

Keywords: Tin, tungsten, U-Pb dating, geochemistry, metallogenesis, Nanling

INTRODUCTION

Cassiterite (SnO₂), the most economically important tin (Sn)-bearing mineral, is generally mined from primary magmatic-hydrothermal deposits that are spatially and temporally associated with highly differentiated granites (Heinrich 1990; Cheng et al. 2019; Zhu et al. 2021). Accurately determining the timing and duration of precipitation of cassiterite is essential to understanding Sn-ore mineralization processes and thus generating genetic models that can aid in prospecting for rare large tin deposits (Yuan et al. 2018). Given its tetragonal, rutile-type structure, cassiterite typically has a high U-Pb ratio as well as a high closure temperature (Zhang et al. 2011, 2017; Neymark et al. 2018). These characteristics give it high resistance to post-ore hydrothermal alteration (Plimer et al. 1991; Hu et al. 2021). Due to their similarities to Sn⁴⁺ with respect to ionic charges, radii, and coordination numbers, trace elements such as Hf, Zr, Sc, Ta, Nb, Ti, Fe, Mn, In, U, and W are able to substitute for Sn in cassiterite either directly or through a coupled substitution mechanism. These elements can be used to trace the cassiterite growth environment as well as the source of mineralizing fluids (Schmidt 2018; Cheng et al. 2019; Bennett et al. 2020; Lehmann 2021; Wu et al. 2021).

The southern Hunan Province, located within the western Nanling metallogenic belt, is one of the most important W-Sn metallogenic regions in China (Mao et al. 2007; Hu et al. 2017; Jiang et al. 2020). This province consists of several major Sn-polymetallic deposits, including the Hehuaping, Bailashui, and Xitian deposits [SnO₂ reserves of 140 metric kilotons [Kt], 420 Kt, and 178 Kt, respectively] (Yao et al. 2014; Wang et al. 2014; Li et al. 2019]. Also located within this province are the Dengfuxian (quartz vein-type), Dayishan (greisen-type), Shizhuyuan (greisen-skarn-type), Xianghualing (granite-type), and Jiuyishan (greisen-type) deposits that are the focus of this study. These deposits are spatially and temporally related to highly differentiated granites of mid-Mesozoic (165–150 Ma) age that have experienced pervasive hydrothermal alteration (Sun et al. 2018; Li et al. 2018a, 2018b; Yang et al. 2018; Xiong et al. 2020; Liao et al. 2021; Wu et al. 2021; Zhu et al. 2021). Despite extensive geochronological research, the relative timings of magma emplacement and Sn-polymetallic mineralization in this province are still poorly known—partly because earlier studies used conventional radiometric dating systems that are readily disturbed in mineralized granite systems (e.g., mica Ar-Ar) (Yin et al. 2002; Cai et al. 2012; Wu et al. 2018; Liu et al. 2019; Liao et al. 2021), and partly because few studies