Controls on cassiterite (SnO$_2$) crystallization: Evidence from cathodoluminescence, trace-element chemistry, and geochronology at the Gejiu Tin District

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ABSTRACT

This paper evaluates controls on cassiterite crystallization under hydrothermal conditions based on the textural setting and geochemistry of cassiterite from six different mineralization environments from the world-class Gejiu tin district, southwest China. The cassiterite samples feature diverse internal textures, as revealed by cathodoluminescence (CL) imaging, and contain a range of trivalent (Ga, Sc, Fe, Sb), quadrivalent (W, U, Ti, Zr, Hf), and pentavalent (Nb, Ta, V) trace elements, with Fe, Ti, and W being the most abundant trace elements. Cassiterite Ti/Zr ratios tend to decrease with distance away from the causative granite intrusion, and so has potential to be used as a broad tool for vectoring toward a mineralized intrusive system.

Elemental mapping of cassiterite grains reveals that trace-element concentration variations correspond closely to CL zoning patterns. The exceptions are distinct irregular domains that sharply cut across the primary oscillatory zoning, as defined by the concentrations of W, U, Sb, and Fe. These zones are interpreted to have formed after primary cassiterite growth via fluid-driven dissolution-reprecipitation processes. Zones with low W and U (and Sb) and high Fe are interpreted to have formed during interaction with relatively oxidized fluids in which W and U are stripped from cassiterite due to cation exchange with Fe$^{3+}$. Systematics of W, U, Sb, and Fe partitioning into cassiterite can, therefore, be used as a monitor of the relative oxidation state of the hydrothermal fluid from which cassiterite precipitates.

Cassiterite U-Pb geochronology results obtained by LA-ICP-MS return ages between 77 and 83 Ma, which is consistent with previous geochronology from the region. Ages determined on zones of dissolution-reprecipitation are similar to ages for primary cassiterite growth, indicating a short (<3 m.y.) timespan of hydrothermal activity. These results confirm the potential of U-Pb dating of cassiterite for directly constraining the timing of Sn deposition.

**Keywords:** Cassiterite, cathodoluminescence (CL) imaging, trace element, fluid redox, geochronology

INTRODUCTION

Most of the world’s tin mineralization is thought to be linked to hydrothermal processes associated with highly fractionated and relatively reduced granite bodies (Lehmann 1990; Heinrich 1990, 1995). The most important tin ore mineral is cassiterite (ideally SnO$_2$), which has a tetragonal lattice structure similar to that of rutile, with Sn cations in sixfold coordination with oxygen. As with rutile, cassiterite can accommodate a wide range of trace elements, including Fe, Ti, W, Ta, Nb, Mn, and Sc (Schneider et al. 1978; Moore and Howie 1979; Fig. 1). This trace-element affinity may be used to infer aspects of fluid compositions and mineralization processes, but we have an incomplete understanding of how trace elements are incorporated in cassiterite (Giuliani 1987). Furthermore, like other quadrivalent element-loving minerals (e.g., zircon, rutile, titanite), cassiterite may incorporate U$^{4+}$ much more strongly than Pb$^{2+}$ (Fig. 1), which means that U-Pb dating of cassiterite may be a robust and reliable geochronometer for Sn mineralizing systems. Despite this potential, there has been relatively little comprehensive work on cassiterite geochemistry and geochronology (Gulson and Jones 1992; Yuan et al. 2008; Zhang et al. 2015).

Cathodoluminescence (CL) is a powerful micro-imaging tool for revealing internal textures, zoning, and the distribution of trace elements within minerals (e.g., Rusk and Reed 2002; Götze and Kempe 2008). Titanium, W, Al, and V impurities are considered to be the chief activators responsible for CL in hydrothermal cassiterite, whereas Fe is considered to be a “CL blocker,” causing a lowering of CL intensity (Farmer et al. 1991). Nevertheless, more information about cassiterite CL patterns and their possible link with chemical compositions is needed. In recent years, CL and laser ablation (LA) inductively coupled plasma-mass spectrometry (ICP-MS) analysis have been successfully combined to correlate micro-textures and compositions of various minerals (e.g., Rusk...