Microstructural controls on the chemical heterogeneity of cassiterite revealed by cathodoluminescence and elemental X-ray mapping

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ABSTRACT

Quantitative X-ray element maps of cassiterite crystals from four localities show that Ti, Fe, Nb, Ta, and W define oscillatory zonation patterns and that the cathodoluminescence response is due to a complex interplay between Ti activated emission paired with quenching effects from Fe, Nb, Ta, and W. Sector zonation is commonly highlighted by domains of high Fe, incorporated via a substitution mechanism independent of Nb and Ta. A second form of sector zonation is highlighted by distributions of W separate to the Fe-dominant sector zone. Both sector zones show quenched cathodoluminescence and are indistinguishable under routine SEM CL imaging. For cassiterite already high in Fe (and Nb or Ta), such as in pegmatitic or granitic samples, the internal structure of the grain may remain obscured when imaged by cathodoluminescence techniques, regardless of the presence of sector zonation. Careful petrogenetic assessments using a combination of panchromatic and hyperspectral CL, aided by quantitative elemental X-ray mapping, is a prerequisite step to elucidate cassiterite petrogenetic history and properly characterize these grains for in situ microanalysis. The absence of a clear petrogenetic framework may lead to unknowingly poor spot selection during in situ analyses for geochronology and trace element geochemistry, and/or erroneous interpretations of U-Pb and O isotopic data.

Keywords: Cassiterite, hyperspectral cathodoluminescence, X-ray element mapping, oscillatory zonation, sector zonation

INTRODUCTION

Cassiterite (SnO₂) is the primary economic tin-bearing mineral recovered in various polymetallic systems that include Li-Sn-Ta-(Nb) pegmatites such as the Greenbushes deposit, Western Australia (Partington et al. 1995), Sn-Cu-Pb-Zn skarns such as Gejju, China (Cheng et al. 2013), and Sn-W hydrothermal vein and greisen systems such as Panaquiora, Portugal (Kelly and Rye 1979). It is also a common minor or accessory phase in other mineralized systems such as the In-bearing Pingüino epithermal polymetallic vein system in Argentina (Lopez et al. 2015), the Breves Cu-Au-(W-Bi-Sn) deposit in Brazil (Tallarico et al. 2004), and some intrusion-related Au systems (Thompson et al. 1999). This association of cassiterite with mineral systems enriched in the “critical” metals W, Nb, Ta, Li, and In (Chakhmouradian et al. 2015) makes this mineral a prime target for research, particularly into its development as a multi-process recorder of mineralizing processes.

Cassiterite is known to show complex growth structures, including sector zonation, oscillatory zonation, and microstructures that may reflect late-stage hydrothermal overprinting (Hall and Ribbe 1971; Carr et al. 2017; Wille et al. 2018). A few recent studies have examined cassiterite as a U-Pb geochronometer using in situ analytical techniques, which requires characterization of the internal structure and growth history of each analyzed grain to provide the petrogenetic framework for interpretation. Carr et al. (2017), Zhang et al. (2017), Guo et al. (2018), Neymark et al. (2018), and Cheng et al. (2019) used scanning electron microscope (SEM) panchromatic cathodoluminescence (CL) to image the internal structure of their cassiterite crystals prior to U-Pb analysis. Unfortunately, only a few studies exist that aid in the interpretation of CL imaging of cassiterite for this purpose (Hall and Ribbe 1971; Farmer et al. 1991; Wille et al. 2018).

In the present study, the chemical basis for zonation patterns in cassiterite is examined by incorporating panchromatic cathodoluminescence imaging and hyperspectral cathodoluminescence mapping with EPMA X-ray element mapping. With these analytical tools, the basis is provided for the interpretation of primary growth structures such as oscillatory and sector zonation, as well as microstructures that may reflect secondary processes like recrystallized (healed) fractures, post-crystallization diffusion fronts and dissolution-reprecipitation reactions. We find that sector zonation imparts a significant control on W and Fe uptake and distribution within cassiterite crystals, and that panchromatic CL imaging alone does not reveal the internal structure of cassiterite grains that have high Fe, Ta, Nb, or W. Because of this, it is important that a combination of CL and quantitative elemental X-ray maps are acquired to properly characterize the microstructure and petrogenetic history of a cassiterite sample prior to in situ microanalysis.

BACKGROUND

Cassiterite crystallizes in the tetragonal system, class 4/mmm (ditetragonal dipyramidal), space group P4/2/mnm, and has unit cell parameters a = 4.7382(4) Å and c = 3.1871(1) Å (Bolzan et al. 1997). It is a member of the rutile structure group of M4O2...