Tin isotopes via fs-LA-MC-ICP-MS analysis record complex fluid evolution in single cassiterite crystals

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ABSTRACT

Tin isototope geochemistry of cassiterite may allow for reconstructing the fluid evolution of tin ore deposits. Here, we present cathodoluminescence (CL) imaging, trace element, and in situ Sn isotope compositions of two cassiterite crystals from an early and a relatively late stage of ore formation of the Xiling vein-style Sn deposit, southeastern China, by femtosecond laser ablation multi-collector inductively coupled plasma mass spectrometry (fs-LA-MC-ICP-MS). Our results show that the early-stage cassiterite from a high-temperature feldspar-stable hydrothermal environment has core, mantle, and rim zones with a systematic decrease in δ124/117Sn3161A (relative to the Sn standard NIST 3161 A) from +0.38 ± 0.06‰ in the crystal core to –0.12 ± 0.06‰ (2 SE) in the mantle zone. This isotopic evolution, also paralleled by a decrease in Ta content by two orders of magnitude, suggests a fluid batch evolving toward isotopically lighter Sn. The very rim zone of this crystal has an intermediate tin isotope composition at about +0.05‰ δ124/117Sn3161A combined with elevated Ta, suggestive of a second fluid batch. The late-stage cassiterite crystal from a muscovite-stable hydrothermal environment has a core with an evolved Sn isotope composition at about –0.15‰ δ124/117Sn3161A combined with low Ta, and a rim with heavier Sn isotope compositions up to +0.30 ± 0.08‰ δ124/117Sn3161A and higher Ta contents. As for the early-stage crystal, two different fluid batches must be involved in the formation of this crystal. Our pilot study highlights the advantage of spatially resolved analysis compared to conventional, solution Sn-isotope analysis of bulk cassiterite crystals. The Sn isotope variations at the microscale reveal the complexity of cassiterite crystal growth by a combination of closed- and open-system fluid evolution and isotope fractionation.

Keywords: Xiling, tin ore deposit, cassiterite, trace-element mapping, in-situ Sn isotope

INTRODUCTION

Cassiterite [SnO2] is the most important ore mineral in tin deposits and can form in magmatic and hydrothermal systems over broad P-T-X conditions (Jackson and Helgeson 1985a, 1985b; Heinrich 1990). Individual cassiterite crystals commonly show distinct zonation patterns in optical (Cheng et al. 2019), cathodoluminescence (CL) or backscatter images, and corresponding microchemical features, indicating changes in physico-chemical conditions during their growth process.

Tin has 10 stable isotopes, and investigations of the Sn isotope composition revealed‰-level variations in natural materials, including meteorites (Creech and Moynier 2019) and Sn ore deposits (Hauksson et al. 2010; Yamazaki et al. 2013; Schulze et al. 2017; Yao et al. 2018); and even more significant variations between magmatic rocks from the Earth and the Moon (Wang et al. 2018, 2019a). The first MC-ICP-MS reconnaissance studies by Haustein et al. (2010) and Yamazaki et al. (2013) observed significant differences in tin isotope composition among cassiterite samples from different localities. The latter study identified a range in δ124/120Sn3161 of –0.44 to +0.38 (corresponding to δ124/120Sn3161 of +0.11 to +0.93) in cassiterite from Eastern Asia. A similar range was also observed by Brügmann et al. (2017) in cassiterite from European and Rwanda tin ore deposits. Yao et al. (2018) showed that the tin isotope composition of cassiterite from global tin deposits (with δ124/116Sn3161 of 0.48 ± 0.62‰, 1σ) is consistently less fractionated than paragenetically later stannite [Cu4FeSnS4] formed at a lower temperature (with –1.47 ± 0.54‰, 1σ). This isotopic shift has been attributed to the oxidation of Sn2+ in solution and concomitant precipitation of heavy-Sn-enriched cassiterite (SnO2 with Sn4+), resulting in residual dissolved Sn with lighter isotopic composition, which is expressed in the more negative δ124/116Sn values of later-formed stannite. Theoretical and experimental studies suggest that Sn isotope fractionation can be caused by redox reactions and liquid-