

Tin isotopes as geochemical tracers of ore-forming processes with Sn mineralization

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ABSTRACT

Tin is a key strategic metal and indispensable in the high-tech industry. Constraining the source of the mineralizing fluids, their pathways, and subsequent ore-forming process is fundamental to optimizing tin exploration and efficient mining operations. Here, we present trace element analysis, LA-ICP-MS mapping, and the first systematic high-precision *in situ* Sn isotope analysis of cassiterite from several tin deposits (i.e., Weilasituo, Baiyinchagan, Maodeng Sn-polymetallic deposits) in northeast China using UV-*fs*-LA-ICP-MS. We show that the distribution of trace elements in cassiterite from these localities reflects crystallization under disequilibrium conditions with coexisting fluids or melts, and it suggests intense fluid-rock reactions. Among the three deposits, cassiterite from the Maodeng Sn-Cu deposit has the heaviest weighted mean Sn isotope composition, with $\delta^{124/117}\text{Sn}$ values ranging from $0.11 \pm 0.04\text{‰}$ to $0.62 \pm 0.08\text{‰}$. The Baiyinchagan Sn-Ag-Pb-Zn deposit displays the lightest isotope composition with $\delta^{124/117}\text{Sn}$ values ranging from $-1.43 \pm 0.06\text{‰}$ to $-0.50 \pm 0.04\text{‰}$. While the Weilasituo Sn-W-Li-polymetallic deposit shows the largest spread in $\delta^{124/117}\text{Sn}$ values, ranging from $-0.66 \pm 0.05\text{‰}$ to $0.59 \pm 0.03\text{‰}$. The Sn isotope variability in these natural cassiterites is attributed to Sn isotope fractionation associated with the diversity of Sn mineralization pathways and different physicochemical conditions. Furthermore, the $\delta^{124/117}\text{Sn}$ values of cassiterite from the Maodeng and Baiyinchagan deposits gradually decrease from early to late mineralization stages, suggesting that they were generated by Rayleigh fractionation during progressive mineral precipitation from a hydrothermal fluid. In contrast, heavy Sn isotope values in late-stage Weilasituo cassiterites are likely a result of disequilibrium fluid-rock interaction with external, wall-rock-derived fluids. Our results reveal that liquid-vapor partitioning or fluid-rock interaction may have more influence on Sn isotope fractionation between cassiterite and evolving ore-forming fluids than do magmatic differentiation, pH, pressure, and temperature during the formation of tin deposits. According to the tin isotopic data obtained so far from this study and published previously, we observe no relationship between the Sn isotope composition of cassiterite and the age of mineralization or tectonic setting. However, cassiterite displays heavier Sn isotope compositions than coexisting stannite (Cu_2FeSn_4) regardless of the deposit type and depth of emplacement, suggesting that the redox state may influence Sn isotope fractionation. More importantly, we first recognize a general shift toward light Sn isotope compositions in cassiterite associated with decreasing Ti/Zr ratios, suggesting that Sn isotopes can be a robust tool for identifying the source of the mineralization. Furthermore, based on our Sn isotope data together with previous studies of fluid inclusion, we propose that the dominant Sn(II) species occur in early ore mineralization systems, then shifts to the Sn(IV) species in late stage due to redox change or higher Cl⁻ activity. Tin isotopes may be a robust tool to trace the mineralization center and fluid pathways and to ascertain the mechanisms of metal precipitation.

Keywords: Fluid-rock interaction, liquid-vapor partitioning, kinetic Rayleigh fractionation, *in situ* Sn isotope, Sn deposits