Helvine-danalite mineralogy of the Dulong Sn-Zn polymetallic deposit in southeast Yunnan, China

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ABSTRACT

Southeastern (SE) Yunnan is a major Sn polymetallic province of China, with the Dulong large Sn-Zn polymetallic deposit (in the Laojunshan orefield) being one of the most representative deposits. Our recent work had first identified helvine-group minerals in this deposit. These minerals mainly occur in massive sphalerite ores, and coexist with sphalerite, pyrrhotite, biotite, talc, cassiterite, and fluorite. Raman spectroscopic, X-ray diffraction (XRD), scanning electron microscopic (SEM), and electron probe microanalysis (EPMA) analyses indicate that these helvine-group minerals are oscillatory-zoned helvine-danalite. Both the helvine and danalite zones are mixed with varying proportion of the other helvine-group end-member, and our studies indicate that the oscillatory zoning was formed mainly by periodic fluctuations of the fluid physicochemical conditions (notably $f_{O_2}$ and $f_{S_2}$), but less related to the variation of the fluid Mn, Fe, and Zn contents. The helvine zone was likely formed in a higher $f_{S_2}$ but lower $f_{O_2}$ environment than the danalite zone. In this study, we present the first LA-ICP-MS in situ trace element data for the helvine-danalite minerals from Dulong, and the results indicate that the helvine has considerably high contents and a wide range of trace elements. The helvine is rich in Ca, Al, Sc, and Y, while the danalite is rich in Sn and P (reaching thousands of parts per million). Such trace element enrichments are likely controlled by their respective ionic size and chalcophile behavior. Meanwhile, the $f_{O_2}$ and $f_{S_2}$ conditions during the zoning formation may have also influenced the trace element distributions: trace elements may have mainly entered the helvine-group minerals by substituting into the M-sites in $M_4[BeSiO_4]_3S$, for instance Al, Sc, and Y substitute for Mn, and Sn and Mg for Fe and Zn. It is noteworthy that the helvine and danalite zones are all HREE-enriched and have distinct negative Eu anomalies. This may be related to the high fluid F-Y-P contents during the mineral formation. High-F-Y fluids can readily incorporate HREEs into helvine-group minerals, and phosphates incorporate HREEs more readily in alkali fluids. Europium occurs as Eu$^{2+}$ in the fluid, causing the negative Eu anomalies observed. We have also identified grains of cassiterite in the helvine-group minerals and its coexisting sphalerite. U-Pb dating on these cassiterite grains yielded 86.5 ± 1.6 Ma, coeval with the reported sulfide mineralization age. This indicates that both the Be and Sn-Zn polymetallic mineralization occurred in the Cretaceous, and may have been products of the Late Yanshanian Laojunshan magmatic-hydrothermal activity. Considering the close relations with many W(-Be) deposits nearby (e.g., Nanyangtian, Saxi, and Maka), the Laojunshan orefield may also have substantial Be mineralization potential.

Keywords: Helvine-group minerals, physicochemical environment, major and trace element compositions, LA-ICP-MS, cassiterite U-Pb age, Dulong Sn-Zn polymetallic deposits

INTRODUCTION

Beryllium is a lithophile rare metal (Goldschmidt 1932), with its upper crustal abundance (~2.1 ppm) being around 30 times its abundance in the primitive mantle (~0.07 ppm) (Taylor and McLennan 1995). Beryllium minerals are commonly found in hydrothermal deposits associated with granitic pegmatites, skarns, and alkaline and (sub-)volcanic rocks. In nature, Be minerals mainly comprise silicates and aluminosilicates, among which beryl, bertrandite, and helvine-group minerals have industry value (Grew and Hazen 2014). Helvengroup minerals are important Be minerals, which have the general formula $M_4[BeSiO_4]_3S$ with $M$ = Mn (helvite), Fe (danalite), or Zn (genthelvite). The crystal structure belongs to sodalite-type, in which the [SiO$_4$] and [BeO$_4$] tetrahedra are interlinked into four- or six-membered rings (Hassan and Grundy 1985; Nimis et al. 1996). It is generally considered that helvite is formed in granites or granitic pegmatites, especially in their intrusive contact zones or endoskarns. Danalite is commonly formed in skarn or contact metamorphism-related deposits and granite or pegmatite. Genthelvite is considered to be the rarest helvengroup minerals, and its presence is only documented in calc-alkaline