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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_{S_2} and f_{O_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