

Evolution of the Mo-HREE carbonatite deposits in the Lesser Qinling Orogen: insights from in-situ geochemical investigation of calcite and sulfate

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The Early Mesozoic Huanglongpu and Huangshui'an carbonatites in the Lesser Qinling Orogen are unique since they are associated with economic molybdenite mineralization with abundant quartz, and relatively enriched in HREE. The carbonatites are composed of dominant calcite, quartz, sulfate (barite-celestine series), K-feldspar, and minor sulfides (molybdenite, galena, pyrite, sphalerite), REE minerals (monazite, bastnasite, parasite, aeschynite and allanite) and pyrochlore.

$\delta^{13}\text{C}$ (-4.78 to -6.93‰) and $\delta^{18}\text{O}$ (7.10 to 9.48‰) for the Lesser Qinling carbonatites generally plot within the primary carbonatite field. Bulk rock compositions display strong enrichments of U, Pb, Mo and HREE compared to typical carbonatite. In-situ $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios of calcite overlap that of sulfate for both the Huanglongpu and Huangshui'an carbonatites, whereas the latter (0.70579-0.70640) is slightly enriched compared to the former (0.70498-0.70582). Calcite displays variable chondrite-normalized REE patterns, with the $(\text{La}/\text{Yb})_{\text{CN}}$ ratios (0.30-12.9) and REE abundances (323-3840 ppm) decreasing from early to late mineralization stages. In addition, the calcite with HREE enrichments of 69.2-386 ppm is the dominant mineral that controls the HREE budget of these carbonatites. Sulfate shows an extremely LREE-enriched pattern [$(\text{La}/\text{Yb})_{\text{CN}} > 5677$] with REE contents ranging from 706 to 4027 ppm.

Combined with other trace element abundances (e.g., Pb) within calcite, the variable REE contents can be explained by distinct mineralization at different evolution stages. Early-stage fractional crystallization of sulfides and REE-minerals results in the decreasing of REE and Pb within calcite, which is followed by the sulfide (galena and molybdenite) dominated mineralization stage that simply decrease Pb without changing of REE contents for calcite. The late-stage mineralization of sulfate, sulfide and REE-minerals induces the depletion of LREE and Pb and enrichment of HREE as recorded in calcite.