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Fluid Chemistry Governs Selective Rare Earth Elements Enrichment in Granites

CHAOXI FAN[1,2], CHENG XU[1] AND DANIEL E. HARLOV[2]

[1]Peking University

[2]GFZ German Research Centre for Geosciences

Compared to both global granitoids and regional counterparts, granitic bedrocks hosting South China's ion-adsorption rare earth element (REE) deposits exhibit higher REE enrichment (Fig. 1), with heavy-REE (HREE)-type granites displaying divergent enrichment trends compared to Light-REE (LREE) deposits. LREE enrichment in granites (e.g., Guangxi biotite granite) is primarily driven by late-stage magmatic autometasomatism rather than conventional fractional crystallization. Despite sharing differentiation indices (Rb/Sr >10, Eu/Eu* <0.3) with REE-poor granodiorites (e.g., Zudong), LREE-rich granites lack correlations between ΣREE and Eu anomalies, invalidating plagioclase-dominated fractionation models. Instead, F-rich hydrothermal fluids during final magma crystallization replace primary REE-bearing minerals (e.g., allanite) with secondary fluorocarbonates (e.g., synchysite-(Ce)), selectively concentrating LREEs while preserving original REE patterns. Isotopic coherence (εNd(t)) between secondary minerals, primary phases, and whole-rock confirms a closed-system process, excluding external fluid inputs. This autometasomatic enrichment is further supported by mantle-derived volatiles (F, Cl) that lower solidus temperatures, prolonging fractionation without directly contributing REEs.

In contrast, heavy-REE (HREE) enrichment necessitates open-system fluid interactions. The Zudong granitoid complex exemplifies this: HREE-rich phases (muscovite granites) exhibit decoupled Nd-Hf isotopes, high zircon $\delta^{18}O$ (>7.5‰), and positive εHf(t), signaling external fluids from low-temperature altered oceanic sediments. These slab-derived F^--rich fluids efficiently mobilize HREEs via fluoride complexes, imprinting negative Ce anomalies (Ce/Ce* ≈ 0.8) characteristic of marine sediments. Subsequent groundwater infiltration introduces CO_3^{2-}, driving a two-stage redistribution. At high temperatures (≥400°C), alkaline carbonate fluids (pH ~8.5) transport LREEs as hydroxyl-carbonate complexes, leaching them from the system. Rapid cooling (≤200°C) and pH shifts destabilize HREE complexes, precipitating them as nanocrystals, resulting in LREE-depleted and HREE enriched patterns. This mechanism aligns with other regional HREE deposits and is corroborated by calcite-REE associations and apatite $\delta^{18}O$ depletion(Fig.2), reflecting meteoric water mixing.

The selective enrichment of LREEs and HREEs in granites hinges on fluid chemistry and physicochemical conditions. LREE retention relies on fluoride complexation in magmatic-hydrothermal systems, while HREE mobilization demands externally sourced ligands (CO_3^{2-}) and dynamic thermal-pH gradients.This fluid-centric model overturns magmatic differentiation paradigms, highlighting how ligand speciation (F^- vs. CO_3^{2-}), fluid provenance, and reactive pathways govern REE fractionation.