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Enrichment mechanism of heavy rare earth elements in magmatic-hydrothermal titanite: Insights from SXAS/XPS experiments and first-principles calculations and implications for regolith-hosted HREE deposits

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ABSTRACT

Heavy rare earth elements (HREE), as critical materials for the global transition to a low-carbon economy, are mostly supplied by regolith-hosted ion adsorption REE deposits formed from the weathering of granites. Magmatic-hydrothermal titanite of pronounced HREE enrichment in granites has been suggested to play an important role in forming HREE-dominated regolith-hosted deposits. However, the crystal-chemical mechanism and geological process responsible for HREE enrichment in titanite remain unknown. In this study, we investigated two texturally distinct types of HREE-enriched titanite (titanite I and II) in granites from the Gucheng regolith-hosted HREE deposit in South China. Secondary ion mass spectrometry (SIMS) U-Pb dating of rutile associated with titanite I and II yielded similar ages of 101.0 ± 1.7 and 97.9 ± 6.2 Ma, respectively, supporting HREE remobilization during auto-metasomatism. Microbeam synchrotron X-ray absorption spectroscopic analyses show that titanite I and II have distinct Y *K*-edge X-ray absorption near-edge structure spectra. The best-fit results of Y *K*-edge extended X-ray absorption fine structure data suggest that titanite I and II have a Y-O first shell with coordination numbers and distances of 7.8 and 7.2 Å and 2.31–2.51 Å and 2.30–2.47 Å, respectively. Measured Y 3*d* and Dy 3*d* X-ray photoelectron spectroscopic data also support different Y,HREE-O first shells between titanite I and II. These results suggest that Y^{3+} and REE^{3+} occupy the 7-coordinated Ca site via three substitutions $(Y,REE)^{3+} + (Al,Fe)^{3+} \leftrightarrow Ca^{2+} + Ti^{4+}$, $2(Y,REE)^{3+} + \square_{Ca} \leftrightarrow 3Ca^{2+}$, and $2(Y,REE)^{3+} + O^{2-} \leftrightarrow 2Ca^{2+}$. First-principles calculations and the lattice strain model predict preferential uptakes of Y^{3+} and $HREE^{3+}$ as the $(Y,HREE)O_8$ polyhedra arising from the latter substitution mechanism at the Ca site in titanite. Moreover, we link the $2Y^{3+} + O^{2-} \leftrightarrow 2Ca^{2+}$ substitution in titanite to highly oxidized and HREE-enriched melts/fluids originating from the subducted slab. These findings further support our previous suggestion that the crystallization of HREE-enriched titanite in granites plays an important role in forming HREE-dominated regolith-hosted deposits.

Keywords: Critical minerals, HERE-enriched titanite, synchrotron XAS, XPS, uptake mechanism, regolith-hosted REE deposit