

CHEMISTRY AND MINERALOGY OF EARTH'S MANTLE

Ab initio calculations of uranium and thorium storage in CaSiO₃-perovskite in the Earth's lower mantle

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ABSTRACT

Earth's mantle convection is powered in part by the radiogenic heat released by the decay of ²³⁸U, ²³⁵U, ²³²Th, and ⁴⁰K. We present ab initio calculations of uranium and thorium incorporation in CaSiO₃-perovskite with and without aluminum, and propose that aluminous calcium silicate perovskite is the likely host of uranium and thorium in the lower mantle. At 15 GPa, the enthalpies of solution into aluminum-free CaSiO₃-perovskite are 10.34 kJ/mol for U⁴⁺ and 12.52 kJ/mol for Th⁴⁺ in SiO₂ saturated systems, while the enthalpies are 17.09 kJ/mol and 19.27 kJ/mol, respectively, in CaO saturated systems. Coupled substitution of U⁴⁺ and Th⁴⁺ with aluminum is thermodynamically favored, with the enthalpies of solution negative for U⁴⁺ and near 0 kJ/mol for Th⁴⁺ throughout the stability field of CaSiO₃-perovskite. Therefore, U incorporation into CaSiO₃-perovskite is spontaneous in the presence of aluminum while Th forms a near ideal solid solution, implying these elements are potentially compatible with respect to partial melting in the transition zone and lower mantle. Furthermore, the solid solution reactions of U⁴⁺ and Th⁴⁺ are broadly similar to each other, suggesting a restriction on the fractionation of these actinides between the upper and lower mantle. U and Th compatibility in the presence of Al has implications regarding actinide transport into the deep mantle within subducting slabs and the geochemical content of seismic anomalies at the core-mantle boundary.

Keywords: Density functional theory, calcium-silicate perovskite, lower mantle mineralogy, uranium, thorium