

CHEMISTRY AND MINERALOGY OF EARTH'S MANTLE

## **Ab initio calculations of uranium and thorium storage in CaSiO<sub>3</sub>-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 <sup>238</sup>U, <sup>235</sup>U, <sup>232</sup>Th, and <sup>40</sup>K. We present ab initio calculations of uranium and thorium incorporation in CaSiO<sub>3</sub>-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 CaSiO<sub>3</sub>-perovskite are 10.34 kJ/mol for U<sup>4+</sup> and 12.52 kJ/mol for Th<sup>4+</sup> in SiO<sub>2</sub> saturated systems, while the enthalpies are 17.09 kJ/mol and 19.27 kJ/mol, respectively, in CaO saturated systems. Coupled substitution of U<sup>4+</sup> and Th<sup>4+</sup> with aluminum is thermodynamically favored, with the enthalpies of solution negative for U<sup>4+</sup> and near 0 kJ/mol for Th<sup>4+</sup> throughout the stability field of CaSiO<sub>3</sub>-perovskite. Therefore, U incorporation into CaSiO<sub>3</sub>-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 U<sup>4+</sup> and Th<sup>4+</sup> 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