CHEMISTRY AND MINERALOGY OF EARTH’S MANTLE

Ab initio calculations of uranium and thorium storage in CaSiO$_3$-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 $^{238}$U, $^{235}$U, $^{232}$Th, and $^{40}$K. We present ab initio calculations of uranium and thorium incorporation in CaSiO$_3$-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$_3$-perovskite are 10.34 kJ/mol for U$^{4+}$ and 12.52 kJ/mol for Th$^{4+}$ in SiO$_2$ saturated systems, while the enthalpies are 17.09 kJ/mol and 19.27 kJ/mol, respectively, in CaO saturated systems. Coupled substitution of U$^{4+}$ and Th$^{4+}$ with aluminum is thermodynamically favored, with the enthalpies of solution negative for U$^{4+}$ and near 0 kJ/mol for Th$^{4+}$ throughout the stability field of CaSiO$_3$-perovskite. Therefore, U incorporation into CaSiO$_3$-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$^{4+}$ and Th$^{4+}$ 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

INTRODUCTION

Earth’s heat is from two primary sources: secular cooling of the planet from primordial sources and radiogenic heat dominated by the breakdown of $^{238}$U, $^{235}$U, $^{232}$Th, and $^{40}$K. Uranium and thorium are the source of the majority of radiogenic mantle heat at present (Arevalo et al. 2009), therefore constraining the distribution and storage of U and Th in the mantle has first-order control on the heat budget of the planet.

Estimates of the mantle’s uranium and thorium budget vary depending on the compositional model used, with low estimates of 12(2)–15.4(18) ppb U and 43(4)–51.3(44) ppb Th (Šrámek et al. 2013; Javoy and Kaminski 2014) based on CI-chondrites and E-chondrites and consistent with mantle geoneutrino fluxes, to high estimates of 20(4) ppb U and 80(12) ppb Th (McDonough and Sun 1995) estimated from peridotite melting relationships relative to chondrite models for the bulk silicate earth. These differences suggest that variation in bulk mantle U and Th and U/Th ratio compared to those inferred from surface melting relationships may arise as a result of deep processes forming or preserving deep mantle reservoirs.

A consequence of uncertainty in the total U and Th budget of the mantle and the distribution within the mantle is subsequent uncertainty of the fraction of the heat budget that results from secular cooling vs. radiogenic heating (e.g., Korenaga 2008; Arevalo et al. 2009; Javoy and Kaminski 2014), with an impact on the interpretation of the Urey ratio, the ratio of Earth’s heat production to surface heat loss, an important factor in interpretation of mantle dynamics. A hidden reservoir not sampled by surface volcanism is often employed to explain differences between Earth’s composition as determined by mantle sampling at the surface and chondrite models (Korenaga 2008). Such deep reservoirs may persist from the earliest history of the planet due to fractionation of material upon solidification of a magma ocean (Labrosse et al. 2007) or develop through time from present-day recycling and incomplete mixing of crustal material enriched in incompatible elements (Samuel and Farnetani 2003).

U and Th are incompatible in near-surface mantle melting due to their high ionic charge and large ionic radius (Beattie 1993). Because oxygen fugacity decreases with depth (Frost and McCammon 2008), U and Th are both expected to adopt the 4+ state in the deep mantle (Wood et al. 1999). Of the lower mantle mineral phases, CaSiO$_3$-perovskite is able to accommodate large cations such as U, Th, and rare earth elements, with its large A site occupied by the Ca$^{2+}$ cation (Taura et al. 2001). Indeed, U and Th are compatible with CaSiO$_3$-perovskite (Corgne et al. 2005; Corgne and Wood 2002), in which the distribution between mineral and melt increases from a peridotite to MORB bulk composition (Hirose et al. 2004). In contrast, U and Th are incompatible with other lower mantle mineral phases, such as bridgmanite (MgSiO$_3$)