Ab Initio Calculations of Uranium and Thorium Storage in CaSiO$_3$-Perovskite in the Earth’s Lower Mantle

Samuel N. Perry$^1$, Jeffrey S. Pigott$^2$, and Wendy R. Panero$^{1,*}$

$^1$School of Earth Sciences, Ohio State University, 274 Mendenhall Laboratory, 125 South Oval Mall, Columbus, OH, 43210, U.S.A

$^2$Department of Earth, Environmental, and Planetary Sciences, Case Western Reserve University, Cleveland, OH, 44106, U.S.A

*E-mail: panero.1@osu.edu

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. Further, 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.
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 $^{238}\text{U}$, $^{235}\text{U}$, $^{232}\text{Th}$, and $^{40}\text{K}$. 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 versus 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$_3$) and ferropericlase ((Fe,Mg)O) (Corgne et al., 2005, Walter et al., 2004). Although CaSiO$_3$-perovskite is estimated to compose no more than 8 vol% of the lower mantle (Irifune, 1994), it is the main host of U and Th in the lower mantle (Corgne et al., 2005).

Synthesis experiments of U and Th solutions have failed to incorporate U into Al-free CaSiO$_3$-perovskite (Gréaux et al., 2012) yet aluminous CaSiO$_3$-perovskite can contain up to 4 at% of U (Gautron et al., 2006) and up to 3.8 at% of Th (Gréaux et al., 2012). As the molar ratio of Al to actinide is about 2 to 1 in these samples, this suggests a coupled substitution of 1 actinide defect on the Ca$^{2+}$ A-site results in a net +2 charge on that site, referred to hereafter as $\text{Act}_{\text{Ca}}\cdot$ in Kröger-Vink notation (Act=actinide), and 2 Al$^{3+}$ defects on 2 Si$^{4+}$ neighboring B-sites generating a net -1 charge for each defect, or 2(Al$_{\text{Si}}$') (Gréaux et al., 2012; Gautron et al., 2006).
Although previous studies have proposed this substitution as the mechanism of actinide incorporation in Ca-perovskite, thus far no direct simulations have been presented as supporting evidence. We focus on aluminum as the most abundant minor component in CaSiO$_3$-perovskite (e.g. Kesson et al., 1994; Kesson et al., 1996). Without such associated actinide defects, a brownmillerite defect ($2\text{Al}_\text{Si}' + \text{V}_\text{O}''$) is favorable over the tschermak defect ($\text{Al}_\text{Si}' + \text{Al}_\text{Ca}'$) (Akber 2003), indicating the mismatch between $\text{Al}^{3+}$ with the Ca-site. Therefore, this approach considers the environment in which $\text{Al}^{3+}$ on the Si-site is enhanced and charge compensated by the effective loss of an oxygen vacancy.

To test this hypothesis, we present the results of ab initio calculations of U and Th oxides and orthosilicates, and U and Th solid solutions of CaSiO$_3$-perovskite with and without Al. We calculate the enthalpy of solution of the actinide species into CaSiO$_3$-perovskite and model the dissolution of the actinides into the perovskite host over the production of minor phase oxides and silicates. The result of this work informs the interpretation of the formation and preservation of large-scale chemical heterogeneities in the deep mantle.

Additionally, uranium composes about 95% of spent nuclear fuel (Bruno and Ewing, 2006) and is a major part of the annually growing issue of nuclear waste disposal. Perovskite (CaTiO$_3$) has been suggested as a component of Synroc (Ringwood, 1979) and is structurally analogous to the high-pressure CaSiO$_3$-perovskite phase. Thus, our results may also provide information on the use of perovskites in long-term actinide containment.

**METHODS**

We used the Vienna Ab initio Simulation Package (VASP) to relax each structure and to calculate the internal energy and pressure of each phase as a function of volume. All density functional theory (DFT) calculations were done using the generalized gradient approximation...
(GGA) with the projector-augmented wave method (PAW) (Kresse and Joubert, 1999; Kresse and Furthmüller, 1996). PAW potentials were employed to allow for accurate description of the localized \( d \)- and \( f \)-electrons in U and Th.

The DFT+U method (Dudarev et al., 1998) was employed to approximate the \( 5f \) electrons more accurately in uranium. Due to the strong electron correlation in uranium, specific care was taken to avoid relaxation to metastable states (Dorado et al., 2009). The total energy is

\[
E_{\text{DFT+U}} = E_{\text{DFT}} + E_{\text{Hub}} - E_{\text{dc}}
\]

where \( E_{\text{DFT}} \) is the base GGA description of the energy, \( E_{\text{Hub}} \) is the Hubbard term accounting for electron-electron interaction, and \( E_{\text{dc}} \) is a double-counting correction (Dorado et al., 2009). \( E_{\text{dc}} \) is described as

\[
E_{\text{dc}} = \frac{U}{2} N(N-1) - \frac{J}{2} \sum \sigma N_{\sigma}(N_{\sigma}-1)
\]

where \( U \) is the on-site Coulomb repulsion, \( J \) is the on-site interaction, and \( N \) is the sum of the electron orbitals (Dorado et al., 2009; Liechtenstein et al., 1995). We adopt values of \( U=4.50 \) eV and \( J=0.51 \) eV for uranium (Geng et al., 2007; Dudarev et al., 1997). We did not use the DFT+U method for the thorium calculations, as the addition of the \( U \) energy term has been found to produce a negligible effect owing to the lack of \( 5f \) electrons. (Song et al., 2013).

Enthalpy, \( H \), is then calculated as

\[
H = E_{\text{DFT+U}} + PV
\]

Where \( E_{\text{DFT+U}} \) is the internal energy as described in eqn 1, \( V \) is the volume of the calculated structure, and \( P \) is pressure.

The crystal structures of all relevant phases were relaxed with 900 eV cutoff energy, starting from their experimentally or theoretically determined unit cells and atomic positions (Downs and Hall-Wallace, 2003; Wyckoff 1963; Wang et al., 2010; Taylor and Ewing, 1978;
Fiquet et al., 1999; Richet et al., 1988). The Monkhorst-Pack k-point meshes were 4x4x4 for the actinide bearing phases, 16x16x16 for the CaO phases, 2x2x2 for CaSiO$_3$-perovskite and its solid solutions, 8x8x8 for SiO$_2$ and Al$_2$O$_3$. Cutoff energies and k-point meshes were chosen so that all calculations converged to within 0.02 eV per unit cell and a localization of the Th- and U-bonding electrons about each atom to 5%.

Tetragonal CaSiO$_3$-perovskite (I4/mcm) (Shim et al., 2002; Caracas et al., 2005) and solid solutions with U and Th were modeled using a 2x2x1 (79–80 atom) supercell, the minimum cell size required to calculate the enthalpy of each defect (eqns 5–11). Cubic CaSiO$_3$-perovskite was not modeled as previous diamond-anvil cell (DAC) experiments have reported CaSiO$_3$-perovskite becoming tetragonal with the incorporation of Al and U or Th (Gréaux et al., 2012; Gréaux et al., 2009; Gautron et al., 2006), a necessary consideration for modeling the incorporation of actinides in the most stable configuration. Furthermore, CaSiO$_3$-perovskite is the only lower mantle phase experimentally observed incorporating large trace element cations in any substantial amount (Corgne et al., 2005). Therefore, we do not consider at this point the incorporation of U and Th into bridgmanite, ferropericlase and post-perovskite, and instead focus strictly on modeling the energetics of actinide incorporation into CaSiO$_3$-perovskite.

We consider two possible charge-balanced defect mechanisms: $\text{Act}_{\text{Ca}}^{++} + \text{V}_{\text{Ca}}^{2+}$ and $\text{Act}_{\text{Ca}}^{++} + 2(\text{Al}_{\text{Si}})$, where $\text{V}$ is a Ca$^{2+}$ vacancy defect, representative brackets to the solid solution between pure and highly aluminous CaSiO$_3$-perovskite. Alternative charge balance mechanisms were not modeled as either ionic radii (Shannon and Prewitt, 1969) differed too much to be representative of the lowest energy configuration (eg. $\text{Act}_{\text{Ca}}^{++} + \text{Ca}_{\text{Si}}^{2+}$) or the substitution mechanism was not realistic in context of the saturated environment we were modeling ($\text{Act}_{\text{Ca}}^{++} + \frac{1}{2}\text{V}_{\text{Si}}^{3+}$). In the first case, we assume that the $\text{Act}_{\text{Ca}}^{+}$ and $\text{V}_{\text{Ca}}^{2+}$ defects are on adjacent Ca sites. In the second case, we
assume that each $\text{Al}^{3+}$ replaces $\text{Si}^{4+}$ adjacent to the $\text{Act}_{\text{Ca}^{2+}}$ defect. To confirm that the defects in
the 2x2x1 supercell (1.25 at% Act) are non-interacting due to the periodic boundary conditions
and that the energy we calculate can be attributed solely to each actinide defect reaction, two
configurations of the 2($\text{AlSi}^\prime$) were modeled in a 2x2x2 supercell (160 atoms; 0.625 at% Act) at
the gamma point. The difference in enthalpy between the two supercell sizes is less than 15
J/mol, thus the 2x2x1 is sufficient to describe the energy of reaction of actinide incorporation: for
concentrations at or below this level, the enthalpy of solution is in the dilute limit. Implicit in
this approach is to neglect other defects potentially active in CaSiO$_3$ perovskite. We address
these two to establish the degree to which vacancies on the Ca-site associated with the actinide
defect can be active.

We also model ThO$_2$, UO$_2$, ThSiO$_4$, and USiO$_4$ to evaluate phase stability as a function of
pressure and for use in calculating the perovskite defect enthalpy. At high pressures, the fluorite-
structured ActO$_2$ oxides ($Fm\overline{3}m; Z = 4$) undergo a phase change to the cotunnite-type (PbCl$_2$)
structure ($Pnma; Z = 4$) (Idiri et al., 2004), with some evidence for the existence of a $Pbca$ high-
pressure phase of the ActO$_2$ oxides (Gréaux et al., 2008). The actinide silicates are isostructural
with zircon (ZrSiO$_4$) ($I\overline{4}1/amd; Z = 4$) at ambient pressure, but do not undergo the same
transitions at high pressure. USiO$_4$ becomes isostructural to the scheelite structure ($I\overline{4}1/a; Z = 4$
(Bauer et al., 2014; Zhang et al., 2009) and ThSiO$_4$ transforms to huttonite, a monazite-
structured phase ($P2_1/n; Z = 4$) (Bose et al., 2009).

The stability of the silicates relative to the oxides was determined

$$\text{ActSiO}_4 \rightleftharpoons \text{ActO}_2 + \text{SiO}_2$$

(4)
in which SiO$_2$ is calculated as stishovite below 45 GPa and the CaCl$_2$-structured phase above.
The dominance of the $\text{Act}_\text{Ca}'' + V_{\text{Ca}}''$ relative to the $\text{Act}_\text{Ca}'' + 2(\text{Al}_\text{Si}')$ defect is established by comparing the enthalpies of reaction

\[ \text{ActCa}_{14}\text{Si}_{16}\text{O}_{48} + \text{CaO} + \text{Al}_2\text{O}_3 \rightleftharpoons \text{ActCa}_{15}\text{Si}_{14}\text{Al}_2\text{O}_{48} + 2\text{SiO}_2 \]  

(5)

The enthalpy of formation in CaSiO$_3$-perovskite is a function of the stability of the pure actinide phase, and therefore dependent upon the breakdown of the silicate, ActSiO$_4$ to its oxides ActO$_2$ + SiO$_2$, and further a function of the relative saturation of the system with respect to CaO or SiO$_2$. The formation of the $\text{Act}_\text{Ca}'' + V_{\text{Ca}}''$ defect is determined by the relevant reaction,

\[ 16\text{CaSiO}_3 + \text{ActO}_2 \rightleftharpoons \text{ActCa}_{14}\text{Si}_{16}\text{O}_{48} + 2\text{CaO} \]  

(6)

\[ 14\text{CaSiO}_3 + \text{ActO}_2 + 2\text{SiO}_2 \rightleftharpoons \text{ActCa}_{14}\text{Si}_{16}\text{O}_{48} \]  

(7)

\[ 16\text{CaSiO}_3 + \text{ActSiO}_4 \rightleftharpoons \text{ActCa}_{14}\text{Si}_{16}\text{O}_{48} + 2\text{CaO} + \text{SiO}_2 \]  

(8)

\[ 14\text{CaSiO}_3 + \text{ActSiO}_4 + \text{SiO}_2 \rightleftharpoons \text{ActCa}_{14}\text{Si}_{16}\text{O}_{48} \]  

(9)

in which equations (6) and (8) are relevant to CaO saturated systems and equations (7) and (9) are relevant to SiO$_2$ saturated systems.

Analogously, the formation of the $\text{Act}_\text{Ca}'' + 2(\text{Al}_\text{Si}')$ defect is calculated by

\[ 15\text{CaSiO}_3 + \text{ActO}_2 + \text{Al}_2\text{O}_3 \rightleftharpoons \text{ActCa}_{15}\text{Si}_{14}\text{Al}_2\text{O}_{48} + 2\text{SiO}_2 \]  

(10)

\[ 15\text{CaSiO}_3 + \text{ActSiO}_4 + \text{Al}_2\text{O}_3 \rightleftharpoons \text{ActCa}_{15}\text{Si}_{14}\text{Al}_2\text{O}_{48} + 2\text{SiO}_2 \]  

(11)

depending upon the relative stability of equation 4.

**RESULTS**

[Table 1]

We confirm the transition of the fluorite-structured ActO$_2$ oxides to the high-pressure $Pnma$ phase (Fig. 1; Table 1), and find that the suggested $Pbca$ phase (Gréaux et al., 2008) is not stable at any pressure for either actinide oxide. ThO$_2$ will undergo the $Fm\overline{3}m$ to $Pnma$ phase transition at 26.9 GPa and UO$_2$ will experience the same structural transition at 29.2 GPa. At
pressures exceeding ~80 GPa the $Pnma$ phase of ThO$_2$ experiences a structural collapse of the $a$-axis, associated with an expansion of the $b$- and $c$-axis, likely comparable to the ZrO$_2$ post-cotunnite phase change to Fe$_2$P structure (Nishio-Hamane et al., 2015). As we expect a similar phase change for UO$_2$, we therefore limit our results to below 80 GPa. We further confirm the transition of the ActSiO$_4$ silicates to the high-pressure phases of huttonite for ThSiO$_4$ and scheelite (CaWO$_4$) structure for USiO$_4$ (Fig. 1) at 5.1 and 6.4 GPa, respectively.

ThSiO$_4$-huttonite is stable relative to the oxides to 11.1 GPa, above which ThO$_2$ + SiO$_2$ is the stable assemblage. In contrast, sheelite-structured USiO$_4$ is stable relative to oxides to 51.7 GPa (Fig. 2; Table 1). This pressure difference of the breakdown to the oxides represents a potential difference in geochemical behavior of Th and U phases in the transition zone and upper portion of the lower mantle.

The Act$_{Ca}$'' + $V_{Ca}$'' defect in CaSiO$_3$-perovskite is most stable for the calcium vacancy as nearest neighbor to the Act$_{Ca}$'' defect, with little difference in the direction, reflecting the slight tetragonal splitting of the nominal cubic structure. The vacancy compensated U and Th defects expand the unit cell by 0.15% and 0.26%, respectively, at 15 GPa and remains nearly constant over the pressure range of the calculations. The coupled Act$_{Ca}$'' + 2(Al$_{Si}$') defect is also most stable when the defects are clustered together. The enthalpy of the Al$_{Si}$' defects when placed on opposite sides of the Act$_{Ca}$'' defect in the (011) direction (Fig. 3) are within 0.2% of the Al$_{Si}$' defects oriented in the (001) direction. The defects appear to be non-interacting at this concentration, in which the defect enthalpies are negligibly lower than in the 2x2x1 supercell calculation. The aluminum compensated U and Th defects expand the unit cell significantly.
more than the vacancy compensated lattice, with a 2.5% and 2.2% volume expansion at 15 GPa, respectively. As with the vacancy compensated defects, the expansion of the lattice is approximately constant over the pressure range of the calculations.

The Act$_{Ca}^{'''} + 2(Al_{Si}^{'})$ defect is more stable than the Act$_{Ca}^{'''} + V_{Ca}^{''}$ defect (eqn 4; Fig. 4), suggesting that the presence of Al$^{3+}$ in the system plays a critical role in actinide compatibility into the perovskite host. The Th$_{Ca}^{'''} + 2(Al_{Si}^{'})$ defect is 11 kJ/mol more stable than the Th$_{Ca}^{'''} + V_{Ca}^{''}$ defect at ambient pressure, increasing to 30 kJ/mol more stable at 80 GPa. In contrast, the $U_{Ca}^{'''} + 2(Al_{Si}^{'})$ defect is 30–40 kJ/mol more stable than the $U_{Ca}^{'''} + V_{Ca}^{''}$ defect, approximately constant throughout the 0-80 GPa range of the calculations.

Calculation of the formation enthalpies of the Act$_{Ca}^{'''} + V_{Ca}^{''}$ (eqns 6 – 9) and Act$_{Ca}^{'''} + 2(Al_{Si}^{'})$ (eqns 10 – 11) defects, we find the $U_{Ca}^{'''} + 2(Al_{Si}^{'})$ defect is negative at all pressures up to at least 80 GPa, varying between -28 and -9.5 kJ/mol over the pressure range of the calculations, while the Th$_{Ca}^{'''} + 2(Al_{Si}^{'})$ defect is <0.5 kJ/mol above 11 GPa (Fig. 5). Conversely, the vacancy compensated defect has a positive enthalpy that increases with pressure, in which the solution enthalpy of U$^{4+}$ incorporation is between 9 and 14 kJ/mol for all pressures in SiO$_2$-saturated systems, and increases from 14 to 32 kJ/mol from 0 to 80 GPa in CaO-saturated systems. The behavior of Th$^{4+}$ is similar in which reaction enthalpy for the formation of the defect is between 12 and 21 kJ/mol when SiO$_2$-saturated, and increases from 16 to 39 kJ/mol when CaO saturated (Fig. 5).

DISCUSSION
Calculated structures and compressibilities of $\text{ActO}_2$ oxides and $\text{ActSiO}_4$ silicates are broadly consistent with experiment and prior ab initio calculations (Table 1). Differences between our equations of state and previously published calculations are a function of the cutoff energy. We can reproduce the softer equations of state by reducing the cutoff energy to 500 eV, but choose the higher cutoff energy (900 eV) to retain precision in the relative energies between phases to high pressure. All calculations tend to predict a lower pressure of transition relative to the experimentally suggested values, which are all based on room temperature diamond-anvil cell experiments. At room temperature, these measurements can be subject to kinetic barriers or non-hydrostatic stresses (Klotz et al., 2009), which may also explain the differences between calculated and measured results.

Although a low-temperature transition of $\text{ThSiO}_4$ from the zircon structure to the scheelite structure has been suggested (Bose et al., 2009), our calculations instead confirm a transition from thorite to huttonite (Liu, 1982) at approximately 5.1 GPa. We calculate the transition of $\text{USiO}_4$ from coffinite (zircon structure) to the scheelite structure at 6.4 GPa, which is lower than the reported 14 – 17 GPa of previous studies (Bauer et al., 2014; Zhang et al., 2009). The contrast between these and previous computational results appear to reside in the cutoff energy (here 900 eV compared to 610 eV in Bauer et al., 2014) and potentially from the treatment of the Hubbard energy (here 4.5 eV versus 2 eV in Bauer et al., 2014). Too soft a cutoff energy will tend to fail to localize the $f$-electrons about the actinide element.

In the $\text{ActO}_2$-$\text{CaO}$-$\text{SiO}_2$-$\text{Al}_2\text{O}_3$ system, defect enthalpy decreases with $\text{SiO}_2$ saturation, and becomes spontaneous to the extent that $\text{CaSiO}_3$-perovskite forms with minor $\text{Al}_2\text{O}_3$ (Fig. 5). Mantle pyrolite and basalt assemblages show that the distribution of $\text{Al}_2\text{O}_3$ between $\text{CaSiO}_3$-perovskite and bridgmanite significantly favors the bridgmanite phase, with a partition

"Always consult and cite the final, published document. See http://www.minsocam.org or GeoscienceWorld"
coefficient, $D_{\text{Ca-SiO}_2}$ of $0.1-0.2$ over the pressure and temperature range of the lower mantle (Nishio-Hamane et al., 2007). Therefore for a mantle with $\sim4$ wt% Al$_2$O$_3$, this suggests $\sim0.5$ wt% Al$_2$O$_3$ in the calcium phase, consistent with measurements in pyrolitic and basaltic compositions to the core mantle boundary (e.g. Kesson et al., 1994; Kesson et al., 1998). Our results suggest incorporation of U$^{4+}$ and Th$^{4+}$ is more favorable in an environment with excess Si and Al. Even in the presence of aluminum, while the reaction enthalpy with Th$^{4+}$ is nearly ideal, U$^{4+}$ reactions are more negative throughout the stability field of CaSiO$_3$-perovskite (Fig. 5), with the defect enthalpy of U$^{4+}$ 18 kJ/mol lower than Th$^{4+}$ at 15 GPa and 10 kJ/mol at 80 GPa. However, the U$^{4+}$ and Th$^{4+}$ coupled substitutions are broadly similar, implying similar incorporation behavior into the perovskite host.

**IMPLICATIONS**

Melt-crystal partitioning measurements of U and Th in CaSiO$_3$-perovskite are made at relatively low pressures (Taura et al., 2001; Corgne and Wood, 2002; Hirose et al., 2004; Corgne et al., 2005), yet equilibration in a deep magma ocean potentially occurs at significantly greater pressure than those employed in these experiments, potentially as deep as the base of the mantle (Labrosse et al., 2007). The reaction enthalpy of U and Th with aluminous CaSiO$_3$-perovskite is roughly constant in the solid state between 0 and 80 GPa. As the melt structure changes slowly under the conditions of the lower mantle (de Koker et al., 2008), this suggests that the melt/mineral partitioning is likely to remain compatible and applicable through the lower mantle. However, the static calculations presented here exclude direct consideration of configurational and vibrational entropy from the defect reactions. However, as the defects are the same between the two systems, the configurational entropic contributions will be identical for Th and U incorporation in CaSiO$_3$-perovskite, and the vibrational effects should be minimally different.
from Th- and U-free perovskites for trace concentrations. The effects of configurational entropy, $S_{\text{config}}$, will be to stabilize the Gibbs free energy of the defect reaction, $G_{\text{rxn}}$, through $G_{\text{rxn}} = H_{\text{rxn}} - T S_{\text{config}}$ in equal proportions for U and Th, and therefore the conclusions are unchanged. Moreover, these results clarify the effect of actinide incorporation in CaSiO$_3$ with excess alumina: The increase in Al-defects will enhance the dissolution of the actinide through additional possible configurations. Therefore, the concentration-dependent defect population will be driven not by the actinide concentration but by the alumina concentration. We cannot, however, exclude the possibility of further phase changes in UO$_2$ and ThO$_2$ at pressures in excess of 80 GPa that would change their behavior. As these are reference phases in determining the enthalpies of reaction, any first-order phase transitions will affect the solubility of U and Th into CaSiO$_3$-perovskite.

Subducting slabs are saturated in SiO$_2$-stishovite below 300 km and enriched in aluminous phases (Irfune and Ringwood, 1993), such that CaSiO$_3$-perovskite forms in environments mostly likely to dissolve U$^{4+}$ and Th$^{4+}$. Deeply subducted oceanic lithosphere hosting CaSiO$_3$-perovskite is therefore a likely phase for transporting U and Th into the lower mantle through retention of actinides already present in enriched continental sediments. Remnants of ancient slabs enriched in heat producing elements near the core mantle boundary (CMB) could potentially be a geochemical source of large low-shear-wave velocity provinces (LLSVPs) beneath Africa and the Pacific, enriched in heat producing elements through sequestration of crustal material (White, 2015). Furthermore, these results imply that the LLSVPs could have formed due to preferential U and Th incorporation into CaSiO$_3$-perovskite via fractional crystallization as a basal magma ocean solidified (Labrosse et al., 2007).
These results may further provide guidance of the design of geologic radioactive waste disposal in Synroc (Ringwood et al., 1979). As perovskite (CaTiO$_3$) and CaSiO$_3$-perovskite both incorporate large cations into their A-site (Corgne and Wood, 2002; Corgne et al., 2003), these calculations suggest similar substitution mechanisms to be at work in CaTiO$_3$ at ambient pressure. Therefore, the compatibility of U into aluminous CaSiO$_3$-perovskite at high pressures may suggest that Synroc storage of ~1 at% uranium and transuranium actinides in CaTiO$_3$ can be stabilized through charge-coupled defects including 3+ cations such as Al in the system.

ACKNOWLEDGMENTS

Support to SNP from the Ohio State Undergraduate Research Scholarship, the Friends of Orton Hall fund grant and the Columbus Rock and Mineral Society scholarship. Further support for this research comes from NSF EAR 09-55647 and NSF EAR-PF 14-52545 to WRP and JSP, respectively. All calculations were run at the Ohio Supercomputer Center, under computing award PAS0238-1 to WRP. We thank Bethany Chidester, Alexandre Corgne, and Razvan Caracas for their insightful reviews of this manuscript and their constructive feedback.

REFERENCES CITED


FIGURE CAPTIONS

**Figure 1.** Pressure induced phase transitions in ActSiO$_4$ (Act = Th, blue; Act = U, red) zircon structure to monazite and scheelite structures (dash dot), in ActO$_2$ $Fm3m$ to $Pnma$ (solid), and the disfavored $Pbca$ phase (dash).

**Figure 2.** The breakdown of ActSiO$_4$ (Act = Th, blue; Act = U, red) to the binary oxides ActO$_2$ + SiO$_2$ (stishovite). Huttonite (ThSiO$_4$) decomposes to oxides at 11.1 GPa, scheelite-structure USiO$_4$ persists to lower mantle pressures and breaks down at approximately 51.7 GPa.

**Figure 3.** The structures of CaSiO$_3$-perovskite with Act$_{Ca}^{''''}$ + $V_{Ca}'''$ defects (left) and Act$_{Ca}^{''''}$ and $2(Al_{Si'})$ defects (right): blue octahedra are SiO$_6$ units, light blue octahedra are Al$_{Si}O_6$, blue-gray sphere are Ca$^{2+}$ atoms, and the green sphere is the Act$_{Ca}^{''''}$ defect.

**Figure 4.** The exchange between the Act$_{Ca}^{''''}$ + $V_{Ca}'''$ and Act$_{Ca}^{''''}$ + $2(Al_{Si'})$ defects according to equation 4 (Act = Th, blue; Act = U, red)

**Figure 5.** The enthalpy ($H$) of defect formation for the Act$_{Ca}^{''''}$ + $2(Al_{Si'})$ and Act$_{Ca}^{''''}$ + $V_{Ca}'''$ reactions (Act = Th, blue; Act = U, red). Phase transformations in the oxides and silicates are marked according to a = ThSiO$_4$ ($I4_1/amd$) to ThSiO$_4$ ($P2_1/n$), b = USiO$_4$ ($I4_1/amd$) to USiO$_4$ ($I4_1/a$), c = ThSiO$_4$ ($P2_1/n$) to ThO$_2$ ($Fm3m$) + SiO$_2$, d = ThO$_2$ ($Fm3m$) to ThO$_2$ ($Pnma$), e = USiO$_4$ ($I4_1/a$) to UO$_2$ ($Pnma$) + SiO$_2$, f = CaO (B1) to CaO (B2).
| Parameter | ThO₂ (Fm3m) | | | ThO₂ (Pnma) | | | ThSiO₄ (I4₁/amd) | | | ThSiO₄ (P2₁/n) |
|-----------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
|           | Thorianite  | Thorite      | Huttonite   |              |              |              |              |              |              |
|           | Theory      | Experiment  | Theory      | Experiment  | Theory      | Experiment  | Theory      | Experiment  |
| V₀(Å³)    | 177.22(18)  | 175.63(3)   | —           | 166.5(3)    | 327.2(2)    | 321.48      | 302.9(4)    | 297.14      |
|           | 178ᵇ        | 174.9ᶜ      | —           | 167.0ᵇ      | 302ᶜ        | —           | —           | —           |
|           | 178ᵇ        | 174.9ᶜ      | —           | 167.0ᵇ      | 302ᶜ        | —           | —           | —           |
| K₀(GPa)   | 189(2)ᵃ     | 198(2)d     | 177(4)ᵃ     | 176.3(15)ᵃ  | —           | —           | 164(4)ᵃ     | —           |
|           | 191ᵇ        | 187.6ᶜ      | 148ᵇ        | 197ᶜ        | —           | —           | —           | —           |
|           | 191ᵇ        | 187.6ᶜ      | 148ᵇ        | 197ᶜ        | —           | —           | —           | —           |
| K⁺        | 4.10(3)ᵃ    | 4.6(3)d     | 4.20(14)ᵃ   | 4.20(3)ᵃ    | —           | —           | 3.5(1)ᵃ     | —           |
|           | 4.5ᵇ        | 7.8ᵇ        | —           | —           | —           | —           | —           | —           |
|           | 4.19ᶜ       | 4.22ᶜ       | —           | —           | —           | —           | —           | —           |
| Stability | 0 to 26.9ᵃ  | 0 to 36ᵈ    | 26.9 to >80ᵃ| 0 to 5.1ᵃ  | 0 to ~6ᵉ   | 5.1 to 11.2ᵃ| ~6 to ~10ᵍ  | —           |
| Range (GPa)| 0 to 26.5ᵇ  | 0 to 27.06ᶜ | 26.5 to ~80ᵇ| 0 to 38ᵇ   | 38 to ~80ᵇ | 0 to 14–17ⁱ | 14–17 up to 45ⁱ| —           |

| Parameter | UO₂ (Fm3m) | | | UO₂ (Pnma) | | | USiO₄ (I4₁/amd) | | | USiO₄ (I4₁/a) |
|-----------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
|           | Uraninite   | Coffinite   | —           |              |              |              |              |              |
|           | Theory      | Experiment  | Theory      | Experiment  | Theory      | Experiment  | Theory      | Experiment  |
| V₀(Å³)    | 167.303ᵃ    | 163.95(4)d  | 158.208ᵃ    | 312.662ᵃ    | 306.25(6)ⁱ  | 277.973ᵃ    | 273.0ᵃ      | —           |
|           | 161ᵇ        | 158.9(5)ⁱ   | 152.3ᵇ      | 284ᶜ        | 305.58(2)ⁱ  | 270ᵉ        | 271.39⁹     | —           |
| K₀(GPa)   | 176.878ᵃ    | 207(2)d     | 151.381ᵃ    | 162.445ᵃ    | 188(4)ⁱ     | 189.599ᵃ    | 274(16)ⁱ    | —           |
|           | 208.3ᵇ      | 192.5ᵇ      | 192.5ᵇ      | 217ᵃ        | 181(5)ⁱ     | 212(1)ⁱ     | 195(6)ⁱ     | —           |
| K⁺        | 3.65021ᵃ    | 4.5(4)d     | 4.77824ᵃ    | 4ᵃ**        | 4ⁱ**        | 4ᵃ**        |              | —           |
| Stability | 0 to 29.2ᵃ  | 0 to ~40ᵈ   | 29.2 to >80ᵃ| 0 to 6.4ᵃ  | 0 to 14–17ⁱ | 6.4 to 51.7ᵃ| 14–17 up to 45ⁱ| —           |
| Range (GPa)| 0 to 38ᵇ   | 38 to ~80ᵇ | 0 to ~15ⁱ   | 0 to 6ᵉ     | 0 to ~15ⁱ   | 15 to >35ⁱ  | ~15 to >35ⁱ | —           |
Notes: aThis study, bWang et al., 2010, cQiang et al., 2014, dIdiri et al., 2004, eBose et al., 2009, fTayler and Ewing, 1978, gLiu 1982, hGeng et al., 2007, iZhang et al., 2009, jBauer et al., 2014

*Fixed to 4.

Table 1. Equations of states of actinide oxide and silicate phases, where $V_0$ is the zero pressure volume, $K_0$ is the zero-pressure bulk modulus, and $K'$ is the pressure derivative of the bulk modulus. No experimental compression equations of state have been measured for the $Pnma$ phases of AO$_2$ or huttonite, and no ab initio equations of state have been calculated for huttonite.
Figure 2.

Δ $H$ (kJ/mol) vs. Pressure (GPa)

- **Act = U**
- **Act = Th**

Silicates more stable

Oxides more stable

$\text{ActSiO}_4 = \text{ActO}_2 + \text{SiO}_2$
Figure 3.
Figure 4.

\[ U_{Ca''} + 2(Al_{Si}) - (U_{Ca''} + V_{Ca''}) \]

\[ Th_{Ca''} + 2(Al_{Si}) - (Th_{Ca''} + V_{Ca''}) \]

\[ \Delta H \text{ (kJ/mol)} \]

CaO (B1) to CaO (B2)

CaSiO$_2$-pv stable

Pressure (GPa)
Figure 5.