



## Ab initio predictions of potassium partitioning between Fe and Al-bearing MgSiO<sub>3</sub> perovskite and post-perovskite

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### ABSTRACT

Ab initio quantum mechanical computations suggest that potassium (K) preferentially partitions into MgSiO<sub>3</sub> perovskite (pv) over post-perovskite (ppv) under lower mantle conditions when charge coupled with trivalent cations of aluminum (Al<sup>3+</sup>) or iron (Fe<sup>3+</sup>). In an Al-bearing MgSiO<sub>3</sub>, the equilibrium constant  $K_D$  increases with pressure, leveling off at  $\sim 33$  at  $\sim 100$  GPa and 3000 K. For an Fe-bearing MgSiO<sub>3</sub>,  $K_D$  slowly increases with pressure reaching a value of  $\sim 8$  at core-mantle boundary (CMB) pressures and 3000 K. Our results imply that a potassium-enriched lowermost mantle layer based on the stability of ppv is unlikely.

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### 1. Introduction

Partitioning of long-lived radioactive isotopes (e.g., <sup>40</sup>K, <sup>235</sup>U, <sup>238</sup>U and <sup>232</sup>Th) in the Earth's interior is important to the thermal evolution of the Earth as radioactive decay provides an important source of energy for mantle dynamics. As a consequence, enriched (or depleted) reservoirs in the mantle influence the energy balance in geodynamics (Buffett, 2002; Labrosse and Jaupart, 2007). The recently discovered transition in MgSiO<sub>3</sub> from perovskite (pv) to post-perovskite (ppv) in the lowermost mantle causes a density increase by  $\sim 1$ –2% between the Mg-endmembers (Murakami et al., 2004; Oganov and Ono, 2004; Shim et al., 2004; Tsuchiya et al., 2004). In addition, as iron preferentially partitions into ppv (Caracas and Cohen, 2005; Mao et al., 2004; Ono and Oganov, 2005), a negatively buoyant Fe-rich ppv layer could play an important role as a stagnant layer. The negative buoyancy of this dense layer is a common trait (2–5% more dense than surrounding mantle) of many proposed thermochemical pile models that accumulate below mantle upwellings (e.g., Davaille, 1999; Lassak et al., 2007).

Such a dense layer at the base of the mantle based on the ppv phase could potentially also provide for a global radiogenically

enriched or depleted zone. Therefore, the partitioning of potassium (K) among the phases of the lower mantle is of central importance to the geochemistry and geodynamics of the deep Earth.

In the crust and upper mantle a number of K-rich phases exist (e.g., feldspars, micas and amphiboles) (Harlow and Davies, 2004) and many experiments on high-pressure potassium-rich phases have been conducted to search for possible lower mantle hosts for K (Ferroir et al., 2006; Guignot and Andraut, 2004; Nishiyama et al., 2005; Sueda et al., 2004; Tutti et al., 2001; Wang and Takahashi, 2000). However, due to the small abundance of potassium,  $\sim 240$  ppm by weight (McDonough and Sun, 1995), a K-rich phase in the mantle is unexpected (Perrillat et al., 2006; Wang and Takahashi, 1999). Instead, potassium should be incorporated into one (or more) of the three major solid solutions in the mantle: iron (Fe) and aluminum (Al)-bearing MgSiO<sub>3</sub> in the perovskite or post-perovskite structure, magnesiowüstite (Mg, Fe)O and calcium silicate perovskite CaSiO<sub>3</sub> (Irifune and Ringwood, 1987; Kesson et al., 1998; Lee et al., 2004; Murakami et al., 2005; O'Neill and Jeanloz, 1990). As potassium is monovalent, to replace a cation in one of the three major solid solutions requires coupling to trivalent cations. The most abundant trivalent cations M<sup>3+</sup> in the Earth are iron and aluminum, both of which we test in this study.

Where potassium resides in the lower mantle may determine where this potentially important internal heat source is located. The pv–ppv phase transition is the only phase transition known in the lower mantle and the ppv bearing D'' layer could consequently provide a distinct global reservoir for heat-producing potassium.

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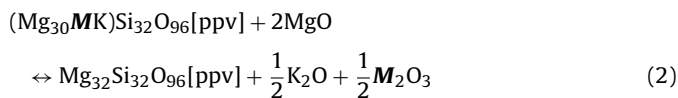
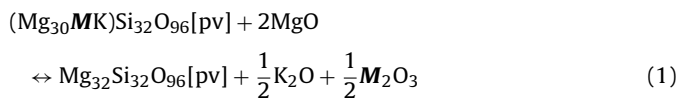
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We here explore this possibility by means of ab initio computations on the incorporation of K into  $\text{MgSiO}_3$  pv and ppv at lower mantle pressures. In order to incorporate monovalent K into the pv or ppv structures, we choose to charge couple  $\text{K}^+$  with  $\text{Fe}^{3+}$  or  $\text{Al}^{3+}$ , the most abundant trivalent cations in the lower mantle that are incorporated readily in  $\text{MgSiO}_3$  pv (Frost and Langenhorst, 2002; Irifune, 1994; Zhang and Oganov, 2006a,b). In the computations we consider Fe and Al-bearing  $\text{MgSiO}_3$  perovskites and their corresponding high-pressure polymorphs, Fe and Al-bearing  $\text{MgSiO}_3$  post-perovskites.

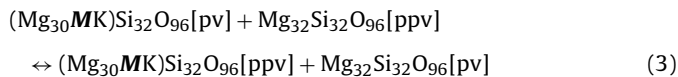
## 2. Methods

### 2.1. Supercell computations and energetics

To investigate K partitioning between pv and ppv we consider the following two reactions composed of oxides and 160-atom silicate supercells:

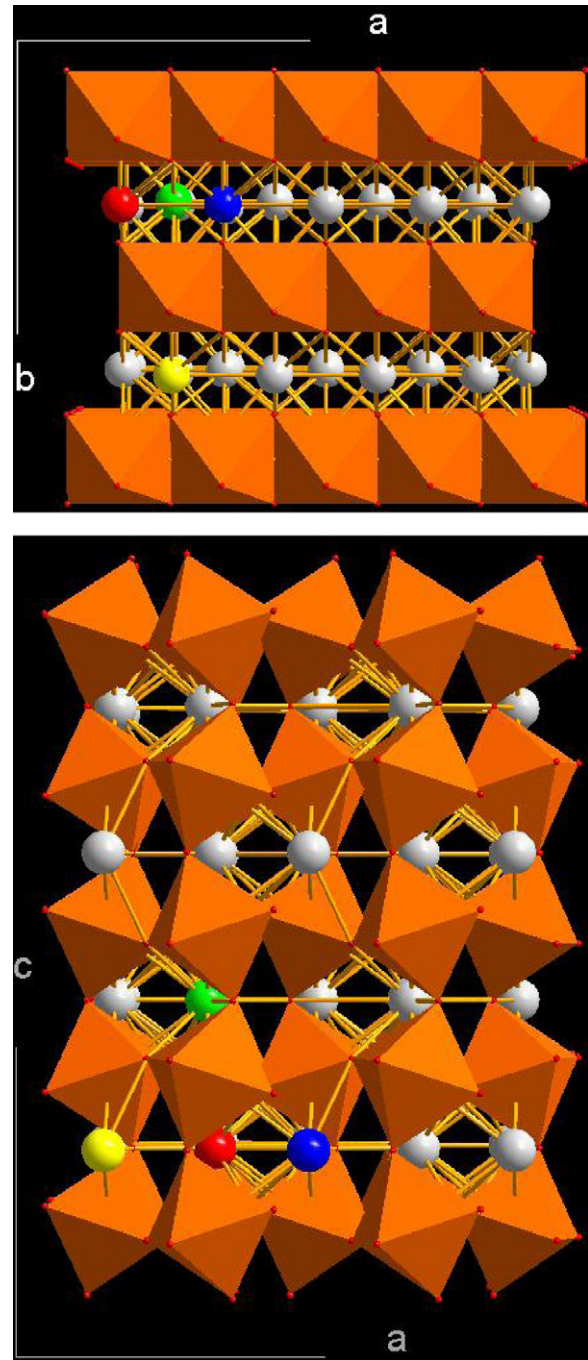


where **M** is Fe or Al. Combining reactions (1) and (2) yields a reaction with only pv and ppv terms:



where the oxide terms cancel. The energetics of this reaction will determine how K partitions between pv and ppv. In our computations for perovskite and post-perovskite, two Mg sites are allowed to have either an iron–potassium or an aluminum–potassium pair that replaces two Mg atoms at adjacent A (Mg)-sites, in order to locally charge balance the  $\text{MgSiO}_3$  based solid solution in pv and ppv. The pv supercells are based on the orthorhombic  $Pnma$  structure and consist of  $2 \times 2 \times 2$  (160 atoms) orthorhombic cells. The ppv supercells are based on the orthorhombic  $Cmcm$  structure and consist of  $4 \times 1 \times 2$  (160 atoms) orthorhombic cells.

The electronic structure and energetics of the supercells used have been calculated by density functional theory (DFT)-based methods. DFT is exact except for the basic approximation for exchange and correlation that describes the many-body interactions of electrons in the system. We use the generalized gradient approximation (GGA) (Perdew et al., 1992) for all of our computations in order to assure compatibility of results as well as to compare with previous computations in the Mg–Fe–Al pv and ppv solid solutions (Akber-Knutson et al., 2005; Ono and Oganov, 2005; Stackhouse et al., 2007). We use the projector augmented wave method (PAW) (Kresse and Joubert, 1999) as implemented in the Vienna Ab initio Simulation Package (VASP) (Kresse and Furthmuller, 1996; Kresse and Hafner, 1993). As we consider high compressions, resulting in hybridization of low-lying electronic states, we chose potentials that treat the following electronic shells as valence: 3p, 3d and 4s for iron; 2p and 3s for magnesium; 3s, 3p and 4s for potassium; 3s and 3p for aluminum and silicon; and 2s and 2p for oxygen. These potentials have been used successfully by previous studies (Oganov and Ono, 2004; Ono and Oganov, 2005; Stackhouse et al., 2007). For the iron-bearing silicates, we perform spin-polarized computations.



**Fig. 1.** (Top) Crystal structure of 160-atom supercell of  $(\text{Mg}_{30}\text{MK})\text{Si}_{32}\text{O}_{96}$  perovskite projected along  $b$ -axis. (Bottom) Crystal structure of 160-atom supercell of  $(\text{Mg}_{30}\text{MK})\text{Si}_{32}\text{O}_{96}$  post-perovskite projected along the  $c$ -axis. The red atom represents K. The three nearest-neighbor **M** atoms are represented by blue, green and yellow, with nn distances increasing. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

To establish the energetics of partitioning we must assure that absolute energies are well converged with respect to computational parameters. For the plane wave computations the critical computational parameters are the cut-off energy for the expansion of the charge density in a plane wave basis ( $E_{\text{cut}}$ ) and the number of reciprocal space vectors at which the Kohn–Sham equations are solved ( $k$ -points). For the 160 atom supercell convergence to within 3 meV/atom for absolute internal energies is achieved with  $E_{\text{cut}} = 1000$  eV and a single  $k$ -point ( $\Gamma$ ).

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