Lower mantle hydrogen partitioning between periclase and perovskite: A quantum chemical modeling

PAVESE, A.[14], BONADIMAN, C.[2], MERLI, M.[3] AND DIELLA, V.[4]

[1]Department of Earth Sciences “A. Desio’’, Università degli Studi di Milano, 20133 Milano, Italy
[2]Department of Physics and Earth Sciences, University of Ferrara, via Saragat 1, 44121 Ferrara, Italy
[3]Dipartimento di Scienze della Terra e del Mare, Università degli Studi di Palermo, 6, 90123 Palermo, Italy
[4]Consiglio Nazionale delle Ricerche, CNR-IDPA, Sezione di Milano, Via Mangiagalli 34, 20133 Milano, Italy

The partitioning of hydrogen (often addressed to as H_2O) between periclase (*pe*) and perovskite (*pvk*) at lower mantle conditions (24-80 GPa) has been investigated, using quantum mechanics, equilibrium reaction thermodynamics and following two H-incorporation models. One is based on the replacements (MSWV) given by $Mg^{2+}\leftrightarrow 2H^+$ and $Si^{4+}\leftrightarrow 4H^+$; the other relies upon substitutions (MSWA) in terms of $2Mg^{2+}\leftrightarrow Al^{3+}+H^+$ and $Si^{4+}\leftrightarrow Al^{3+}+H^+$. H_2O partitioning between the two mentioned phases is considered in the light of Bulk Silicate Earth (BSE) and Layered Mantle (LM) mantle geochemical models, which are set up to bear lower and upper bulk H_2O contents *(BWC*) of 800 and 1500 ppm. ${}_{BWC}K(P,T)_{D,H2O}^{pe/pvk}$, exhibits negligible dependence on *P*, whereas it is remarkably sensitive to *T*, *BWC* and hydrogen incorporation scheme. Both MSWV and MSWA lead to ${}_{BWC}K(P,T)_{D,H2O}^{pe/pvk} \leq 1$. In general, the larger *BWC*, the smaller is ${}_{BWC}K(P,T)_{D,H2O}^{pe/pvk}$. Over the *BWC* range of 800-1500 ppm, MSWV leads to a $<{}_{BWC}K_{D,H2O}^{pe/pvk}>$ (average of ${}_{BWC}K(P,T)_{D,H2O}^{pe/pvk}$ calculated along the *P-T*-paths predicted by geochemical models) that may be ultimately considered as a constant value (0.875). For MSWA, $<{}_{BWC}K_{D,H2O}^{pe/pvk}>$ is more sensitive to *BWC* (and LM over BSE), but its values lie in the rather narrow range 0.610- 0.780. The concentration ratios “partition coefficient”: $C_{H2O}^{pe}/C_{H2O}^{pvk}$,) inferred from $<{}_{BWC}K_{D,H2O}^{pe/pvk}>$ r is estimated to be 0.56. MSWA, in turn, yields a $C_{H2O}^{pe}/C_{H2O}^{pvk}$-trend having a slightly steeper negative slope ($C_{H2O}^{pe}/C_{H2O}^{pvk}$ ratio: 0.6-0.3; *BWC* 500-3000 ppm), but over the interval 800-1500 ppm it may also be considered nearly invariant and as large as 0.47). Combining the results from MSWV and MSWA we propose that, in the *P-T-BWC* range of geochemical interest, the H_2O $^{pe/pvk}$ “partition coefficient” lies in the short interval 0.47-0.56. This implies that water always prefers *pvk* than *pe*.