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Potential docking sites and positions of hydrogen in high-pressure silicates

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ABSTRACT

A method based on an analysis of the Laplacian of the electron density distribution is used to locate positions of nonbonding electron-pairs and favorable docking sites for hydrogen in high-pressure silicates, including stishovite, akimotoite, wadsleyite, ringwoodite, $MgSiO_3$, and $CaSiO_3$ perovskite. In stishovite, model hydrogen positions (h) are located off the shared O···O edge of the octahedra with the Oh vector oriented perpendicular to [001]. In akimotoite, two model positions for hydrogen are found, one along an edge of the MgO_6 octahedron with an Oh vector aligned close to [001] and the other within the face of the MgO_6 octahedra, with Oh vectors oriented perpendicular to [001]. Geometric and electrostatic considerations suggest that both of these sites would require vacant Mg sites. In wadsleyite, potential sites for protonation exist for all O atoms. Hydrogen bonded to O1 resides in a cage-like site with the Oh dipole oriented parallel to [001]. Two symmetrically equivalent sites for hydrogen exist at O2 in a second cage-like structure with Oh vectors aligned approximately along [100]. The calculations also identify potential sites for hydrogen at O3 and O4, but suggest that these could only be occupied by hydrogen if vacancies exist at adjacent Mg sites. Model hydrogen positions in ringwoodite are predicted along O···O edges of the MgO_6 octahedron, and, if occupied, would require vacancies at adjacent Mg sites. $MgSiO_3$ perovskite is distinguished by having only one potential site for hydrogen. The Oh vector lies within the (110) plane and geometric and electrostatic considerations suggest that a vacancy is required at the Mg site if this site is protonated. No localized sites for hydrogen are found in $CaSiO_3$ perovskite. We suggest that non-bonded electron pairs associated with oxide anions involved in octahedral frameworks with tilt angles of less than 180° provide more favorable docking sites for protons than those involved in wider angles. The results from the electron density calculations show very good agreement with available crystallographic and spectroscopic data and demonstrate that the strategy used in this study can be useful in locating protons in Earth materials.