

First Principle Study on Substitution Mechanisms of Water in Ringwoodite

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Abstract: The constitutional water of ringwoodite critically influences the physical and chemical properties, such as the density, composition, elasticity, of ringwoodite and the seismic velocities in the mantle transition zone. In this paper, the first principle method with Long-term Van der Waals correction has been attempted to be used in the field of computational geochemistry for the first time. Comparing with the traditional DFT calculations, the results of this method are much better matched to the experimental measurements. Various water substitution mechanisms in ringwoodite have been simulated and calculated by using Van der Waals corrected method. They include Mg vacancy mechanism ($V_{Mg}'' + 2H_O^*$), Si vacancy mechanism ($V_{Si}''' + 4H_O^*$), and anti-site mechanism ($Mg_{Si}'' + 2H_O^*$). Based on the simulation and calculation of the defect formation energy and related chemical reaction energy, we found that the mechanisms of water substitution in ringwoodite are different under different pressure conditions. At low pressure (0 GPa), the Si vacancy mechanism ($V_{Si}''' + 4H_O^*$) is the most stable one, but water is more favorable to substitute Mg into ringwoodite with the Mg vacancy mechanism ($V_{Mg}'' + 2H_O^*$) at 16 GPa. Both mechanisms are more stable than the anti-site mechanism ($Mg_{Si}'' + 2H_O^*$). In the case of the coupled substitution involving hydrogen plus trivalent elements of Fe^{3+} , Al^{3+} , Sc^{3+} , Lu^{3+} , Y^{3+} , and Nd^{3+} in ringwoodite, the Si vacancy mechanism ($M'_{Si} + H_O^*$) in the system containing Fe^{3+} , Al^{3+} and Nd^{3+} is more stable than the Mg vacancy mechanism ($V_{Mg}'' + M_{Mg}^* + H_O^*$), while the Mg vacancy substitution mechanism in the system containing Sc^{3+} , Lu^{3+} and Y^{3+} is the most stable one.

Keywords: ringwoodite; constitutional water; trivalent cations; incorporation mechanisms