Usage Report for Fiscal Year 2024

Project Title:

Materials under high pressure

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1. Background and purpose of the project, relationship of the project with other projects

Although the oceans cover 71% of the Earth's surface, geologists speculate that a vast amount of water—possibly several times more than what exists at the surface—is trapped within the Earth's interior. However, this water does not exist in liquid form; instead, it is believed to react with and become incorporated into minerals. One key candidate for storing this water is ringwoodite, a mineral abundant in the subduction zone between 410 and 600 km below the surface. Experiments have demonstrated that ringwoodite can absorb significant amounts of water, causing its color to change from transparent to blue. If this hypothesis is confirmed, it would have profound implications for understanding the deep water cycle, which exchanges water through the mantle and back to the surface. This computational project aims to uncover the mechanism behind water's reaction with ringwoodite and the resulting changes in its electronic structure under geological conditions.

2. Specific usage status of the system and calculation method

We conducted first-principles constant-pressure, constant-temperature molecular dynamics simulations to investigate the reaction of water with ringwoodite. The calculations were performed using the VASP program. The model consisted of 128 water molecules confined between two crystalline ringwoodite (Mg_2SiO_4) slabs. The initial setup involved inserting ice VII into ringwoodite, followed by equilibration at 20 GPa and 2500K, replicating the conditions of previous experiments. Multiple trials were necessary to refine the simulation parameters and establish the appropriate conditions. Simulations were performed at 2000K, 2500K and 3000K and 20 GPa. All computations were carried out on the Hokusai supercomputer cluster.

3. Result

The structure of the equilibrated structure (initial structure) is shown in Fig. 1, showing no reaction has occurred in the equilibrium stage.

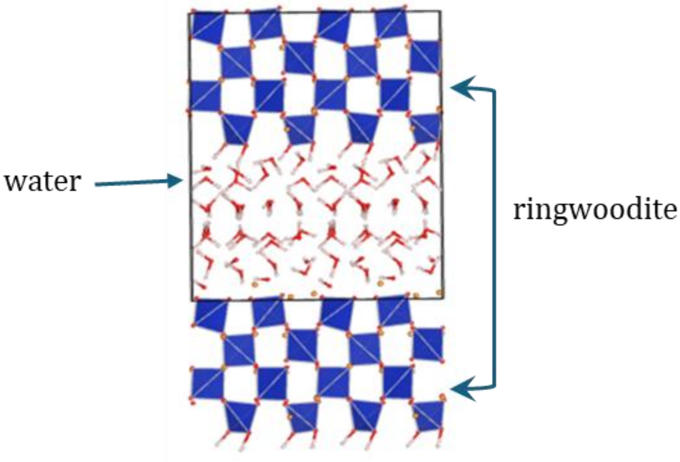

Fig. 1

At 2500K and 3000K at 20 GPa the ringwoodite dissolved in water readily. The results reported below correspond to 20 GPa and 2000K.Longer simulations up to 60 ps were then performed. Interactions between the water and the minerals started to proceed after a few thousand timesteps. The processes is succinctly summarized as follows. A surface Mg migrates into the water layer. The vacancy is quickly filled by a water molecule which dissociated to OH with the H attached to the oxygen of the exposed SiO4 unit. Fig. 2 shows the trajectory of one selected Mg ion during this process. The red circled area shows the formation Si-O..H and the isolated H atom. The "dot" plot of changing colours (from deep-blue to brown) indicates the propagation of the solvated Mg ion from the initial position into the water layer.

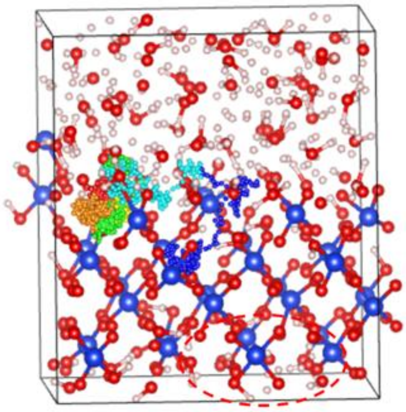

Fig. 2

At longer time, Mg ions situated in the second layer of the ringwoodite start to migrate into the water layer. Fig. 3 shows the trajectory of one selected Mg ion. The vacancy created is quickly filled by an H from the liquid water. The initial migration of the Mg ions into the water layer is very rapid. The "free" Mg then diffuses throughout the liquid. The trajectory of a Mg ion is shown by a "dot" plot with the initial position of the Mg ion coloured in light green in the second layer of Ringwood and progresses to dark green in the water layer. The formed OH bonded to SiO is illustrated in the shade circle in the enlarged region. Notably, the ringwoodite crystalline structure remains largely intact in the bulk even after prolonged simulations at 2000K. However, within the same timescale, a slight increase in temperature to 2500 K leads to the complete dissolution of the structure in liquid water.

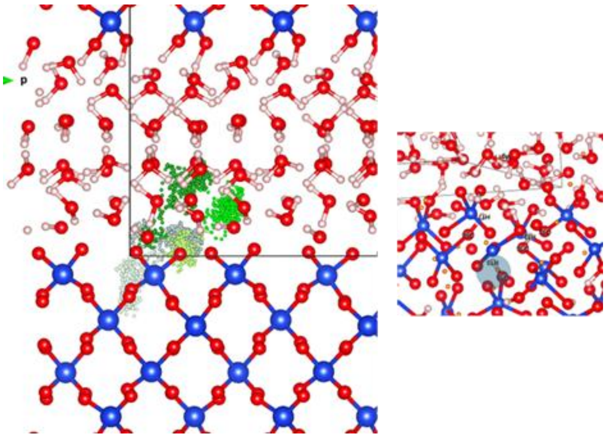

Fig. 3

To examine the electronic structure of the solvation process, the electronic density of states (DOS) are computed at different P-T conditions and compared in Fig. 4

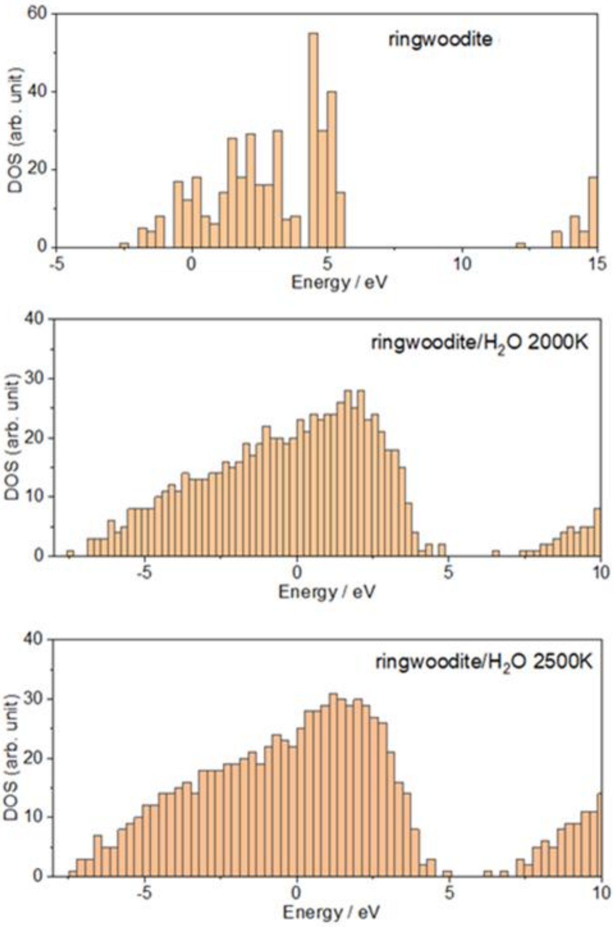

Fig. 4

4. Conclusion

The main results are as follows. (a) There are spontaneous interactions between water and the ringwoodite mineral. The reactions are very facile and proceed rapidly even in the molecular dynamic timescale. (b) The initial process is driven by the dissolution of the Mg ions into liquid water. The vacancy is filled by water molecules which dissociated into OH and H with the formal entity attached to the oxygen of the SiO_4 tetrahedra. (c) Mg ions situated in the second layer migrate into the water and the void is saturated by the OH of water. (d) The gap decreases gradually with the abstraction of Mg ion turning the colour of the crystal from transparent to blue.

The theoretical results reported here substantiate the ease of water absorption by ringwoodite at the conditions of the subduction zone. Furthermore, the calculations reproduced the observed colour change upon hydration.

５.　Schedule and prospect for the future

We wish to (a) further explore the electronic structure of the system, in particular, to compute the absorption spectrum in order to better understand the origin of the colour change associated with the dissolution the ringwoodite. (b) to extend the simulation to detect the conditions for the complete collapse of the crystalline structure.

The project is expected to complete within the twelve months. We shall prepare a publication to report the findings.

６.　If no job was executed, specify the reason.

Fiscal Year 2024 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

[Conference Proceedings]

[Oral presentation]

Part of the results obtained here was presented in an Invited Lecture, “Chemical Processes under Extreme Conditions” at 2024 Goldschmidt Conference, Chicago (USA), Session 2D “Probing Earth and planetary interiors with advanced computational methods”.

[Poster presentation]

[Others (Book, Press release, etc.)]