Hydrogen distribution in chondrodite: a first-principles calculation

Masami KANZAKI

Institute for Planetary Materials, Okayama University, 827 Yamada, Misasa, Tottori 682–0193, Japan

In synthetic hydroxyl-chondrodite and hydroxyl-clinohumite, two hydrogen sites (H1 and H2) are known. However, hydrogen occupying only H1 site has been reported for natural F– and Ti–rich chondrodite and clinohumite. In order to understand hydrogen distribution in these sites, stability of hydrogens at these sites in chondrodite is studied by first-principles density functional theory calculation. For hydroxyl-chondrodite, lowest energy was found when both H1 and H2 sites are half occupied by hydrogens. In this configuration, strong H1–H1 repulsion is avoided, and nearly straight hydrogen bond of O–H1 £ O–H2 is realized. When a half of OH− is replaced with F− or replaced with O2− in the case of Ti–containing systems, hydrogen occupying H1 site is always favored over hydrogen in H2 site so as to form nearly straight hydrogen bond of O–H1–F− (or O2−). Our calculations are fully consistent with the observed structures in both synthetic and natural chondrodite, and revealed that hydrogen distribution in humite group minerals is mostly governed by hydrogen bonding at H1 site.

Keywords: Chondrodite, Clinohumite, Humite group, Hydrogen bonding, First-principles DFT calculation

INTRODUCTION

Natural humite group minerals generally contain both F and OH in the structures. The structures of humite group minerals were made of alternating layers of Mg2n−1Si8 O4n−2 and 2MgO(OH,F), with n = 1, 2, 3 and 4 corresponding norbergite, chondrodite, humite and clinohumite respectively (Fujino and Takéuchi, 1978). Pure hydroxyl phases (chondrodite–OH, clinohumite–OH) have been synthesized under high pressures (Yamamoto and Akimoto, 1977). These hydroxyl phases are regarded as possible hydrous minerals in the upper mantle. Although no pure chondrodite–OH nor clinohumite–OH has been reported in nature, Ti–containing nearly F–free chondrodite and clinohumite derived from mantle xenoliths are known (Aoki et al., 1976). For these Ti–containing chondrodite or clinohumite, OH content is reduced by a substitution mechanism [Mg(OH)2 = TiO2] in MgO(OH) layer (Fujino and Takéuchi, 1978). Many structural refinements of both natural and synthetic humite group minerals have been reported. In terms of hydrogen sites, two hydrogen sites (H1 and H2) are reported for chondrodite–OH and clinohumite–OH with nearly 50% occupancies (Lager et al., 2001; Berry and James., 2001). If H1 site is fully (100%) occupied by hydrogen, short H1–H1 distance is resulted in the structure, and it is generally thought that such configuration is less favored. On the other hand, in natural humite group minerals including chondrodite containing F/(F + OH) > 0.5, hydrogen occupying only at H1 site has been reported (e.g., Ottolini et al., 2000). For Ti–containing chondrodite and clinohumite, again hydrogen occupying only at H1 site was observed (Fujino and Takéuchi, 1978). It should be noted that for these F–rich or Ti–rich cases, short H1–H1 distance configuration is no longer dominant, because of lower OH concentration. Based on classical potential energy calculations of relevant clusters, Abott et al. (1989) correctly predicted hydrogen sites for humite group minerals (i.e., H1 and H2 sites). However, they concluded that hydrogen occupying H2 site is more stable than that of H1 site, and H2 site is further stabilized in F– or Ti–containing systems. This is contrary to previous observations for natural and synthetic humite group minerals. In order to clarify this contradiction, and to further understand stability of hydrogen in H1 and H2 sites in relation with hydrogen bonding in the humite mineral group in general, first-principles calculations of chondrodite–OH and F– and Ti–containing chondrodite–OH are conducted. Griffin et al. (2009) also conducted DFT calculations of chondrodite–OH and clinohumite–OH, but
their major subject was to estimate NMR parameters, and detailed structures and energies for their simulated four configurations were not reported.

**CALCULATION PROCEDURES**

The first-principles density functional theory (DFT) calculation was performed using the QUANTUM ESPRESSO (ver. 5.2.0) package (Giannozzi et al., 2009), similar to our previous studies of Mg–Zn olivine solid solution (Kanzaki and Xue, 2016) and hydrous forsterite (Xue et al., 2017). PBEsol functional PAW-type pseudopotentials (Mg.pbesol-n-kjpaw_psl.0.3.0. UPF, Si.pbesol-n-kjpaw_psl.0.1.UPF, O.pbesol-n-kjpaw_psl.0.1.UPF and H.pbesol-kjpaw_psl.0.1.UPF) from the PSlibrary (Dal Corso, 2014) were used for all calculations. PBEsol functional is intended for solids and surfaces (Perdew et al., 2008). To our experiences (Xue et al., 2017), PBEsol generally reproduces experimental volumes of silicate minerals better than other functionals of generalized gradient approximation (GGA).

For chondrodite–OH, partially occupied H1 and H2 sites should be considered. There are four hydroxyl oxygen (O5) sites in the unit cell, and these are denoted as a, b, c, and d in Figure 1. Site names (e.g., O5) used in this paper are same as those commonly used in structural reports (e.g., Lager et al., 2001). Since H1 and H2 sites pointing in two opposite directions from O5 site, we can randomly assign one of two orientations for each O5 site to mimic partially occupied H1 and H2 sites. This model is denoted here as DORA (dual orientation random assignment) model. Therefore, in the DORA model, there are sixteen (24) possible configurations for chondrodite–OH. All sixteen configurations are considered in the present study. For all systems except Ti-containing chondrodite, single unit cell (not supercell) is considered. In order to distinguish each configuration, it is denoted such as ‘1212’ (order of a, b, c, d, with 1 for H1 site, and 2 for H2 site). Although only some of these configurations keep chondrodite’s original space group (P21/c), we assume that these configurations are existing as local and instantaneous structure, and averaged spatial and temporal distribution will still hold P21/c symmetry.

For F-containing chondrodite (denoted as chondrodite–F/OH), a model with half of the OH replaced with F was used. In this case, OH and F are placed alternatively in the cell, so that no hydrogen bond between H and O2− is formed in this model. Similar treatment was done for Ti-containing system (denoted as Ti-chondrodite–OH), but 1 × 2 × 1 supercell is used for this system. In Ti-rich chondrodite, Ti exclusively occupies M3 site (one of three octahedral sites), and M3 site is locating in Mg(OH) layers (Fujino and Takéuchi, 1978). Therefore, two Mg in M3 site (out of 8 Mg occupying M3 site in the supercell) are replaced with two Ti to mimic reported Ti-rich chondrodite structure, and corresponding OH is replaced with non-hydroxyl oxygen (O2−) at O5 site. Thus, the composition of this model is 2Mg2SiO4 (Mg1/2Ti1/2)[O1/2(OH)1/2]2 or Mg3Si2O6·2 [(Mg3/4Ti1/4) (O2/3(OH)1/3)]. These initial configurations (both cell parameters and atomic coordinates) were fully relaxed at ambient pressure.

The kinetic energy cutoffs for wave functions and charge density, and scf energy convergence threshold were set to 60, 360 and 10−12 Ry, respectively. The Brillouin zone was sampled using the Monkhorst-Pack scheme with a 2 × 4 × 2 grid (2 × 2 × 2 for Ti-chondrodite). Xue et al. (2017) checked these parameters for hydrous forsterite and related hydrous and anhydrous minerals, and concluded that these cutoffs and K point sampling are good enough for structural simulations of hydrous silicates.

**RESULTS AND DISCUSSION**

Figure 2 shows calculated relative enthalpies of 25 configurations (16 DORA model configurations plus additional ones described below) of chondrodite–OH as a function of H2 site occupancy, and Table 1 lists unit cell volumes and relative enthalpies for each configuration. We found that when two nearby H1 sites are occupied (such as 1111 configuration), there are two stable configurations for this short H1–H1 distance as shown in Figure 3a. Experimental hydrogen position at H1 site (Lager et al., 2001) would correspond to an average position of

![Figure 1. Crystal structure of chondrodite–OH viewed from b-axis direction. Blue, red, orange and magenta spheres represent Si, O, Mg and H atoms, respectively. Labels (a–d) are showing hydroxyl oxygen (O5) positions. This example shows optimized structure of 1122 configuration (hydrogens occupying H1 site near a and b, and occupying H2 site near c and d). This and other structures are drawn by VESTA 3 (Momma and Izumi, 2011).](image-url)
these two configurations. They have essentially identical hydrogen bond topology, but OH bonds flipped from each other. These are designated as $\alpha$ and $\beta$ in Table 1 (see Fig. 3a). Since there are two such configurations formed between pairs of $a$–$d$ and $b$–$c$ in the unit cell of 1111 configuration (no hydrogen occupancy in H2 site), four combinations ($\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, and $\beta\beta$) exist as shown in Table 1. Single $\alpha$ or $\beta$ exists for 25 and 50% H2 site occupancies, but none for 75 and 100%.

These $\alpha$ and $\beta$ configurations are responsible for the enthalpy splitting in 0, 25, and upper part of 50% H2 site occupancies as shown in Figure 2. The $\beta$ configuration is always lower in enthalpy (Table 1). In these configurations, two H1–O5 hydrogen bonds are formed (Fig. 3a). The H1–O5 distance and O5–H1–O5 angle are 2.068 Å and 136.2° for $\alpha$, and 2.095 and 135.9° for $\beta$, respectively. H1–H1 distance is 1.521 Å for $\alpha$, and 1.549 Å for $\beta$ (these values are from the optimized structures). Longer H1–H1 distance configuration of latter might explain lower enthalpy of $\beta$. These H1–H1 distances are much larger than those of structure refinements (1.027 Å for chondrodite–OD by Lager et al., 2001) which are calculated from averaged structure, but direct comparison of these values is not valid.

When hydrogen occupying only H1 site (1111) and hydrogen occupying only H2 site (2222) are compared (0 and 100% H2 occupancies respectively), the former is more stable (Fig. 2 and Table 1). Previous studies generally assumed that fully occupied H1 site becomes less stable, because of formation of short H1–H1 distance. Our calculation, however, reveals that the former (1111) is still more stable even if such short H1–H1 penalty exists. In other word, hydrogen occupancy in H2 site is not quite favored at all. If H2 site is occupied, hydrogen forms bifurcated hydrogen bonds with O1 and O2. For the optimized 2222 configuration (hydrogen only occupies H2 site), O5–O1 hydrogen bond distance is 2.804 Å, and O5–O2 distance is 2.772 Å, and O5–H2–O1 and O5–H2–O2 angles are 134.5° and 110.6°, respectively. This bifurcated hydrogen bonds might be responsible for less favored occupation of hydrogen in H2 site.

When both H1 and H2 sites are half occupied by hydrogen, enthalpy values split into three levels (see 50% H2 occupancy in Fig. 2). As noted above, splitting of upper two levels are due to $\alpha$ and $\beta$ configurations. Upper two correspond to structure that is a mixture of 1111 and 2222 configurations (for example, 1221 configuration), and having single $\alpha$ or $\beta$ in the unit cell. Accordingly, the enthalpies are close to average of the end-member configurations. Inspection of optimized structure for lowest enthalpy configurations (e.g., 1122) reveals formation of O5–H1–O5($-\beta$) hydrogen bond configuration in both $a$–$d$ and $b$–$c$ pairs. The configuration around $a$–$d$ pair is shown in Figure 3b. This hydrogen bonding configuration is denoted as $\gamma$ in Table 1. This configuration has lowest energy because short H1–H1 repulsion no longer exists, and O5–H1–O5 forms nearly straight hydrogen

| H2% DORA model | H-bond type* | Cell volume (Å$^3$) | Enthalpy difference (kJ/mol) ** |
|----------------|--------------|--------------------|-------------------------------|
| 0              | 1111 $\alpha$| 367.090            | 24.2                          |
| 0              | 1111 $\beta$ | 366.932            | 23.4                          |
| 0              | 1111 $\alpha\beta$ | 366.933 | 23.4                          |
| 0              | 1111 $\beta\beta$ | 367.023 | 14.9                          |
| 25             | 1112 $\gamma\alpha$ | 367.187 | 15.7                          |
| 25             | 1112 $\gamma\beta$ | 367.154 | 8.7                           |
| 25             | 1112 $\alpha\gamma$ | 367.193 | 15.6                          |
| 25             | 1112 $\beta\gamma$ | 367.169 | 8.6                           |
| 25             | 1211 $\alpha\gamma$ | 367.194 | 15.6                          |
| 25             | 1211 $\beta\gamma$ | 367.160 | 8.7                           |
| 25             | 2111 $\gamma\alpha$ | 367.198 | 15.6                          |
| 25             | 2111 $\gamma\beta$ | 367.160 | 8.7                           |
| 50             | 1212 $\alpha\gamma$ | 365.095 | 51.1                          |
| 50             | 1212 $\alpha\beta$ | 368.970 | 41.6                          |
| 50             | 2112 $\alpha\beta$ | 369.051 | 51.1                          |
| 50             | 2112 $\alpha\beta$ | 368.971 | 41.7                          |
| 50             | 2121 $\gamma\alpha$ | 367.167 | 0.1                           |
| 50             | 2211 $\gamma\alpha$ | 367.190 | 0.0                           |
| 75             | 1222 $\gamma$ | 368.947 | 33.6                          |
| 75             | 2221 $\gamma$ | 368.940 | 33.6                          |
| 75             | 2212 $\gamma$ | 368.940 | 33.6                          |
| 75             | 2122 $\gamma$ | 368.940 | 33.6                          |
| 100            | 2222 $\gamma$ | 370.664 | 66.7                          |

$a$ and $\beta$, short H1–H1 configurations; $\gamma$, O–H1–O5–H2 hydrogen bonding configuration.
* First one is a configuration made by hydrogens in $a$ and $d$ positions, second by $b$ and $c$ positions (Fig. 1).
** Entalpy differences from most stable (lowest) 1122 configuration (−1341.98454 Ry).
bonding as shown in Fig. 3b. H1–O5 distance is 2.047 Å, and O–H1–O angle is 172.6° for 1122 configuration. The cell volumes of such configurations are about 0.5% smaller than those of other configurations as shown in Table 1. Lowering of the enthalpies for 25% and 75% H2 site occupancies is also observed due to realization of γ configuration, but less significant as there is only single γ configuration in the unit cell for these cases (see Fig. 2 and Table 1).

From Figure 2, it is clear that lowest enthalpy can be realized when H1 and H2 sites are half occupied with two O5–H1–O5 hydrogen bonds (γγ) in the unit cell (i.e., 1122, 1212, 2121 and 2211 configurations). This result compares well with previous structural refinements reported for chondrodite–OH (Lager et al., 2001) as described before. However, it should be noted that the diffraction studies have not directly detected O5–H1–O5 hydrogen bonding configuration, as the diffraction technique only gives average structure. Vibrational spectroscopy which is more sensitive to local structure around hydrogen in shorter time scale can be used to confirm this hydrogen bonding configuration.

For natural chondrodite, more than half of OH is replaced with F. As a result, O5–H1–O5–H2 hydrogen bond becomes rare or none in such systems, as nearby O5 is now replaced with F−. No short H1–H1 repulsion is expected in this system. Our calculations for F−-containing chondrodite (chondrodite–F/OH in Table 2) reveal that enthalpy for hydrogen occupying H1 site, thus forming nearly straight O5–H1–F hydrogen bonding, is lower than that of hydrogen occupying H2 site as shown in Table 2. H1–F distance is 1.874 Å, and O5–H1–F angle is 173.2°. The cell volume is smaller for the configuration with hydrogen occupying H1 site than that of H2 site.

Situation is very similar for Ti–containing chondrodite–OH (Table 2) in which F− is now replaced with non-hydroxyl oxygen (O3−) as shown in Figure 4. For this system, corresponding O5 (d in Fig. 4) coordinating to

| Structure     | Configurations | H2% | Cell volume (Å³) | Enthalpy difference (kJ/mol) |
|---------------|----------------|-----|-----------------|-------------------------------|
| CD-F/OH†      | 0              | 361.646 | 0.0            |
| CD-F/OH‡      | 100            | 364.252 | 71.2           |
| Ti-CD-OH†     | 0              | 722.490 | 0.0            |
| Ti-CD-OH‡     | 100            | 729.458 | 181.6          |
| CH-OH         | 1111§          | 0    | 656.215        | 13.9                         |
| CH-OH         | 1122          | 50   | 656.680        | 0.0                          |
| CH-OH         | 2222          | 100  | 660.153        | 68.7                         |

CD, chondrodite; CH, clinohumite.
† F is located at b and d positions (Fig. 1).
‡ Cell volumes for 1 × 2 × 1 supercell.
§ ββ hydrogen bond configuration.
# Enthalpy differences from most stable configuration.
titanium ion is under-bonded state, as this non-hydroxyl O5 is bonded with two Mg and one Ti octahedra, resulting bond strength sum of 4/3. Therefore, this O5 will behave as a hydrogen bond acceptor. The hydrogen in H1 site will form stronger hydrogen bonding with this hydrogen bond acceptor O5. H1–O distance is 1.830 Å, and O5–H1–O angle is 173.2°. H1–O distance is shorter than those in other systems reported in present study, and consistent with expected stronger hydrogen bond. Since all existing structural refinements of F- and Ti-containing chondrodite reported only H1 site, but no H2 site, our calculations are consistent with observations. Apparently, the results of Abott et al. (1989) mentioned before were not accurate enough in terms of relative stability of hydrogens in H1 and H2 sites.

Structure of clinohumite is similar to chondrodite having thicker Mg2n-1SiO4n-2 layer (n = 4) than chondrodite (n = 2). However, hydrogen environment is almost identical. In order to roughly check hydrogen stability, a few selected configurations of clinohumite-OH corresponding to 1111(ββ), 2222 and 1122(γγ) of chondrodite-OH are calculated (Table 2). Lowest enthalpy is obtained for half occupied H1 and H2 sites with straight H1–O–H2 hydrogen bonding configurations, identical to that of chondrodite-OH.

For other humite group minerals, no crystal structure has been reported for synthetic hydroxyl-humite or hydroxyl-norbergite to date, although existence of synthetic ‘humite-OH’ has been reported (Wunder et al., 1995). Our preliminary calculation for ‘norbergite-OH’ with H1 and H2 sites reveals similar trend just like chondrodite-OH and clinohumite-OH. Therefore, half occupied H1 and H2 sites are expected, if these phases are synthesized. However, further detailed calculations and experimental challenge for synthesis of these phases are necessary to confirm this preliminary result.

We note that similar situation might exist for topaz [Al2SiO4(OH,F)2]. Hydroxyl-topaz (called topaz-OH) is stabilized at high pressure, and two hydrogen sites (H1 and H2) nearly half occupied are reported (e.g., Komatsu et al., 2008). For natural F-containing topaz, only single H site has been reported. Although hydrogen local structure is not quite same with chondrodite, our preliminary calculations reveal a trend quite similar to chondrodite. Although more detailed calculations are necessary, hydrogen distribution in topaz could be interpreted in a similar way.

It should be noted that our calculations are at 0 K, and thermal effect is not considered. Actually, Griffin et al. (2009) reported proton exchange between two H sites at room temperature in hydroxyl-chondrodite and hydroxyl-clinohumite from 17O NMR observation. Even so, our present study provides a basis to understand static and dynamic disorders of hydrogen in these minerals.

Based on present first-principles DFT calculations, distribution of hydrogen in H1 and H2 sites in chondrodite can be summarized as follows. For lower OH concentration, hydrogen occupying H1 site and forming straight hydrogen bond with OH–, F– or O2– is favored over hydrogen in H2 site that results in bifurcated hydrogen bonds. If OH content exceeds a half (H/(F + H)), formation of short H1–H1 configuration cannot be avoided if only H1 site is occupied. Partial occupancy of H2 site then becomes more favorable as a result of straight O5–H1–O5–H2 hydrogen bond formation. Therefore, hydrogen bonding at H1 site mainly controls the configuration of hydrogen distribution in chondrodite and other humite group minerals. As demonstrated in this study, first-principles DFT calculation is very useful for understanding hydrogen bonding in hydrous phases.

ACKNOWLEDGMENTS

The author thanks Prof. Xianyu Xue, and two reviewers for constructive comments.

REFERENCES

Abott, Jr, R.N., Burnham, C.W. and Post, J.E. (1989) Hydrogen in humite-group minerals: Structure–energy calculations. American Mineralogist, 74, 1300–1306.

Aoki, K., Fujino, K. and Akagai, M. (1976) Titanochondrodite and titanoclinohumite derived from the upper mantle in the Buell Park kimberlite, Arizona, USA. Contributions to Mineralogy and Petrology, 56, 242–253.

Berry, A.J. and James, M. (2001) Refinement of hydrogen positions in synthetic hydroxyl-clinohumite by powder neutron diffraction. American Mineralogist, 86, 181–184.

Dal Corso, A. (2014) Pseudopotentials periodic table: From H to Pu. Computational Materials Science, 95, 337–350.

Fujino, K. and Takeuchi, Y. (1978) Crystal chemistry of titanian chondrodite and titanoclinohumite of high-pressure origin. American Mineralogist, 63, 535–543.

Giannozzi, P., Baroni, S., Bonini, N., Calandra, M., Car, R., Cavazzoni, C., Ceresoli, D., Chiarotti, G. L., Cococcioni, M., Da- bo, I., Dal Corso, A., Fabris, S., Fratesi, G., de Gironcoli, S., Gebauer, R., Gerstmann, U., Gougoussis, C., Kokalj, A., Lazzeri, M., Martin-Samos, L., Marzari, N., Mauri, F., Marzaroni, S., Paulino, S., Pasquarello, A., Paulatto, L., Sbraccia, C., Scandolo, S., Schauzro, G., Seitsonen, A. P., Smogunov, A., Umari, P. and Wentzcovitch, R.M. (2009) QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. Journal of Physics: Condensed Matter 21, 395502.

Griffin, J.M., Wimperis, S., Berry, A.J., Pickard, C.J. and Ashbrook, S.E. (2009) Solid-state 17O NMR spectroscopy of hydrous magnesium silicates: Evidence for proton dynamics. Journal of Physical Chemistry C, 113, 465–471.

Kanzaki, M. and Xue, X. (2016) Cation distribution in Mg-Zn oli-
vine solid solution: a $^{29}$Si MAS NMR and first-principles calculation study. Journal of Mineralogical and Petrological Sciences, 111, 292-296.

Komatsu, K., Kagi, H., Marshall, W.G., Kuribayashi, T., Parise, J.B. and Kudoh, Y. (2008) Pressure dependence of the hydrogen-bond geometry in topaz-OD from neutron powder diffraction. American Mineralogist, 93, 217–227.

Lager, G.A., Ulmer, P., Miletich, R. and Marshall, W. G. (2001) O-D–O bond geometry in OD-chondrodite. American Mineralogist, 86, 176–180.

Momma, K. and Izumi, F. (2011) VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. Journal of Applied Crystallography, 44, 1272-1276.

Ottolini, L., Câmara, F. and Bigi, S. (2000) An investigation of matrix effects in the analysis of fluorine in huminite-group minerals by EMPA, SIMS, and SREF. American Mineralogist, 85, 89-102.

Perdew, J.P., Ruzsinszky, A., Csonka, G.I., Vydrov, O.A., Scuseria, G.E., Constantin, L.A., Zhou, X. and Burke, K. (2008) Restoring the density-gradient expansion for exchange in solids and surfaces. Physical Review Letters, 100, 136406.

Wunder, B., Medenbach, O., Daniels, P. and Schreyer, W. (1995) First synthesis of the hydroxyl end-member of humite, Mg$_7$Si$_3$O$_{12}$(OH)$_2$. American Mineralogist, 80, 638-640.

Xue, X., Kanzaki, M., Turner, D. and Loroch, D. (2017) Hydrogen incorporation mechanisms in forsterite: New insights from $^{1}$H and $^{29}$Si NMR spectroscopy and first-principles calculation. American Mineralogist, in press.

Yamamoto, K. and Akimoto, S. (1977) The system MgO-H$_2$O-SiO$_2$ at high pressures and temperatures – Stability field for hydroxyl-chondrodite, hydroxyl-clinohumite and 10 Å-phase. American Journal of Science, 277, 288-312.

Manuscript received July 17, 2016
Manuscript accepted October 26, 2016
Manuscript handled by Akira Yoshiasa