Refinement of hydrogen positions in synthetic hydroxyl-clinohumite by powder neutron diffraction

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ABSTRACT

The structure of synthetic hydroxyl-clinohumite [$Mg_7Si_4O_{14} \cdot 2Mg(OH)O$] was refined for a deuterated sample using powder neutron diffraction data and the Rietveld technique [($P2_1/b$; $Z = 2$; $a = 4.7488(1)$ Å; $b = 10.2875(2)$ Å; $c = 13.6967(3)$ Å; $\alpha = 100.63(1)°$; $V = 657.65(2)$ Å^3)]. The H atoms of the hydroxyl groups are disordered over two positions with an occupancy of approximately 0.5. This removes the possibility of a strong H-H interaction that was thought to destabilize the structure. The limited occurrence of hydroxyl-clinohumite in nature is the result of compositional rather than crystal chemical constraints.

INTRODUCTION

The hydroxyl humite minerals have the general formula nMg$_2$SiO$_4 \cdot$Mg(OH)$_2$ where $n = 1$ (norbergite), 2 (chondrodite), 3 (humite), or 4 (clinohumite). They may be viewed as hydrated forms of forsterite and can be described simplistically as comprising forsterite-like blocks and intervening layers of brucite. The presence of titanian chondrodite and titanian clinohumite in kimberlites (McGetchin et al. 1970; Aoki et al. 1976) and the experimentally determined stability fields of the corresponding hydroxyl compounds (Yamamoto and Akimoto 1977; Burnley and Navrotsky 1996; Wunder 1998) indicate that these phases could exist in the upper mantle. Although the importance of these minerals as a repository of mantle water is likely to be limited, it is possible that water may be accommodated as a clinohumite-type defect in olivine (Kitamura et al. 1987). Nominally anhydrous minerals such as olivine may contain the entire water budget of the upper mantle at defect sites (Bell and Rossman 1992; Kohlstedt et al. 1996). The position of the hydrogen atoms in clinohumite is integral to understanding the stability of the hydrated layer. Although the humite structures are otherwise well defined, the hydrogen positions have only been determined approximately from X-ray diffraction studies (Yamamoto 1977; Fujino and Takéuchi 1978; Cámara 1997; Ferraris et al. 2000) and structure energy calculations (Abbott et al. 1989). The orientation and strength of the O-H bond is also important for understanding the infrared hydroxyl stretching bands, which are commonly used to quantify the water content of mantle olivines. This paper reports the first precise determination of hydrogen locations in a humite mineral.

EXPERIMENTAL METHODS

Synthesis

Clinohumite was synthesised at 29 kbar and 830 °C from a 5:2 molar mixture of Mg(OH)$_2$ or Mg(OD)$_2$ and SiO$_2$. Mg(OD)$_2$ was prepared by the addition of D$_2$O to Mg$_3$N$_2$. The OD content was determined to be 87 ± 1% from a comparison of the oscillator strength corrected OD and OH stretching bands in the infrared spectrum. The clinohumite reaction conditions were achieved using a 30 mm piston cylinder apparatus with end-load supplied by a 500 ton press. The sample was contained in a capsule (35×15 mm) machined from Ag rod with a press-on lid that forms a water-tight seal under pressure (Woodland and O'Neill 1997). A graphite heater, pressure medium of NaCl/pyrex/boron nitride, and pyrophyllite end-pieces were used. Around 2.5 g of clinohumite could be produced in each run and 5 g of both the hydrate and deuterate were synthesized. Run times were approximately four hours.

Powder neutron diffraction

Powder neutron diffraction measurements were made on the high-resolution powder diffractometer (HRPD) using thermal neutrons ($\lambda = 1.4930$ Å) from the HIFAR nuclear reactor at the Australian Nuclear Science and Technology Organisation (ANSTO). The minimum instrumental resolution (FWHM) for HRPD is 0.27°. Data were collected using a bank of 24 ^{3}He detectors over the range $0° < 2\theta < 153°$ in 0.05° steps. Structural refinements were carried out for the deuterated sample by the Rietveld method (Rietveld 1969) using the LHPM program (Howard and Hunter 1997), with Voigt peak shapes and a refined background.

RESULTS

The initial model used for refinement of the hydroxyl-clinohumite structure was that proposed for clinohumite by Robinson et al. (1973). The initial positions of the hydrogen

atoms were based on those determined from X-ray Fourier difference maps for hydroxyl-chondrodite (Yamamoto 1977). The atomic coordinates and atomic displacement parameters were refined for each of the atoms present. The occupancies of the two D sites were refined with the average D:H ratio at each site fixed at 87:13 and the total occupancy constrained to be 1.0. These occupancies are strongly correlated with the atomic displacement parameters and so in the final stages of the refinement these parameters were fixed at reasonable values. An excellent fit to the data was obtained (R_P = 3.4%, R_B = 1.6%). Hydroxyl-chondrodite and brucite (identified by the 001 reflection in x-ray diffraction) were present as impurity phases and were included in the refinement, although their atomic parameters were fixed at literature values (Yamamoto 1977; Chakoumakos et al. 1997). Quantitative phase analysis gave 9(1)% hydroxyl-chondrodite and less than 1(1)% brucite by weight.

The crystallographic data obtained from the refinement of the structure of hydroxyl-clinohumite are given in Table 1, while the refined atomic coordinates and isotropic atomic displacement parameters are given in Table 2. Selected bond lengths and hydrogen bonding distances are given in Table 3. The ob-

served, calculated and difference neutron diffraction profiles for hydroxyl-clinohumite are shown in Figure 1.

DISCUSSION

The refined structure of hydroxyl-clinohumite is the same as previously reported for natural clinohumite (Robinson et al. 1973; Ferraris et al. 2000). Chains of edge-sharing MgO_6 octahedra are cross-linked to chains in the same and adjacent layers by SiO_4 tetrahedra (Fig. 2). Two types of MgO_6 octahedra share four edges with other MgO_6 octahedra and two edges with SiO_4 tetrahedra (Mg1, Mg2). There are also two types of MgO_6 octahedra which share two edges with octahedra and one edge with a tetrahedron (Mg3, Mg4), and one octahedron which shares edges with three octahedra and one tetrahedron (Mg5). Both of the two different SiO_4 tetrahedra share all three basal edges with MgO_6 octahedra in the same layer.

Two distinct hydrogen positions are associated with the oxygen O9 with refined occupancies 0.52(2) for D1 and 0.48(2) for D2 (Table 2). The D1 atom points toward a center of symmetry within the brucite-like layer and occupies a cavity defined by two Mg3 octahedra, four Mg5 octahedra and two Si2 tetrahedra. The D2 site is located within an olivine-like block cavity composed of two Mg3 octahedra, two Mg5 octahedra, one Mg2 octahedron and a Si2 tetrahedron.

An extensive hydrogen bonding network is formed between the hydroxyl protons and adjacent oxygen atoms, predominantly in the brucite layers, which stabilizes the structure. The presence of strong hydrogen bonds is reflected in the longer than usual O-D bond lengths of the hydroxyl groups [D1-O9: 1.07(2) Å; D2-O9: 1.08(2) Å]. These values are significantly longer than the 0.958(3) Å observed in brucite (Catti et al. 1995;

TABLE 1. Crystallographic data for hydroxyl-clinohumite

Formula	$Mg_7Si_4O_{14} \cdot 2Mg(OH)O$
Formula weight	621.103
Color	white
D_c (g/cm³)	3.144
2θ range (°)	15.0–145.0
no. of reflns	1496
R_P / R_B (%)	3.4/1.6
Space group	$P2_1/b$ (No. 14)
Z	2
a (Å)	4.7488(1)
b (Å)	10.2875(2)
c (Å)	13.6967(3)
α (°)	100.63(1)
V (Å³)	657.65(2)

Notes: $R_P = \Sigma|y_i(\text{obs})-y_i(\text{calc})| / \Sigma y_i(\text{obs})$, where y_i is the (gross) intensity at the ith step of the profile.
$R_B = \Sigma|I_k(\text{obs})-I_k(\text{calc})| / \Sigma I_k(\text{obs})$, where I_K is the intensity assigned to the Kth Bragg reflection.

TABLE 2. Fractional atomic coordinates and isotropic atomic displacement parameters (B_{iso}) for hydroxyl-clinohumite

Atom	x	y	z	B_{iso}(Å²)
Mg1	0.5	0	0.5	0.5(1)
Mg2	0.495(3)	0.9480(9)	0.2735(8)	0.7(1)
Mg3	0.003(3)	0.1440(8)	0.1711(6)	0.5(1)
Mg4	0.504(3)	0.2523(9)	0.3872(7)	0.9(1)
Mg5	0.492(3)	0.8770(9)	0.0443(6)	0.8(1)
Si1	0.073(3)	0.0666(12)	0.3897(10)	1.0(1)
Si2	0.078(3)	0.1739(10)	0.8341(9)	1.2(1)
O1	0.733(1)	0.0647(5)	0.3892(6)	1.0(1)
O2	0.277(1)	0.4200(5)	0.3881(5)	0.9(1)
O3	0.224(2)	0.1120(8)	0.2932(6)	0.6(1)
O4	0.224(1)	0.1575(5)	0.4869(4)	0.8(1)
O5	0.238(1)	0.3240(6)	0.1638(5)	0.4(1)
O6	0.775(1)	0.9703(6)	0.1644(5)	0.7(1)
O7	0.725(1)	0.2825(7)	0.2637(6)	0.7(1)
O8	0.728(1)	0.2294(7)	0.0715(6)	0.8(1)
O9	0.261(2)	0.0529(10)	0.0596(7)	1.5(2)
D1*	0.098(4)	0.017(2)	0.008(2)	3.0
D2*	0.418(4)	0.088(2)	0.115(2)	3.0

Notes: e.s.d. values in parentheses. Mg1 atoms occupy the special 2d (1/2,0,1/2) site while all the other atoms occupy general 4e sites.
*Refined Occupancy: D1 = 0.52(2); D2 = 0.48(2).

TABLE 3. Selected bond lengths and hydrogen bond distances (Å) with e.s.d. values in parentheses

| Atom1-Atom2	Bond length (Å)	Atom1-Atom2	Bond length (Å)
Mg1- O1 × 2	2.084(2)	Si1-O1	1.613(7)
Mg1-O2 × 2	2.071(2)	Si1-O2	1.666(8)
Mg1-O4 × 2	2.119(2)	Si1-O3	1.647(9)
Mg2-O1	2.130(3)	Si1-O4	1.641(7)
Mg2-O2	2.091(3)	Si2-O5	1.613(7)
Mg2-O3	2.0984	Si2-O6	1.646(6)
Mg2-O5	2.098(7)	Si2-O7	1.642(7)
Mg2-O6	2.046(7)	Si2-O8	1.642(6)
Mg2-O7	2.148(8)		
Mg3-O3	2.050(3)	O9-D1	1.07(2)
Mg3-O5	2.180(4)	O9-D2	1.08(2)
Mg3-O6	2.076(6)		
Mg3-O7	2.173(7)	Hydrogen bonds	
Mg3-O8	2.188(7)	O3 ··· D2	2.58(2)
Mg3-O9	2.046(11)	O5 ··· D2	2.55(2)
Mg4-O1	2.221(3)	O6 ··· D1	2.46(1)
Mg4-O2	2.033(4)	O6 ··· D1	2.75(1)
Mg4-O3	2.197(5)	O8 ··· D1	2.70(1)
Mg4-O4	2.254(4)	O8 ··· D2	2.23(1)
Mg4-O4	2.081(4)	O9 ··· D1	2.01(2)
Mg4-O7	2.061(8)		
Mg5-O5	2.120(9)		
Mg5-O6	2.205(9)		
Mg5-O8	2.104(9)		
Mg5-O8	2.040(9)		
Mg5-O9	2.092(9)		
Mg5-O9	2.073(10)		
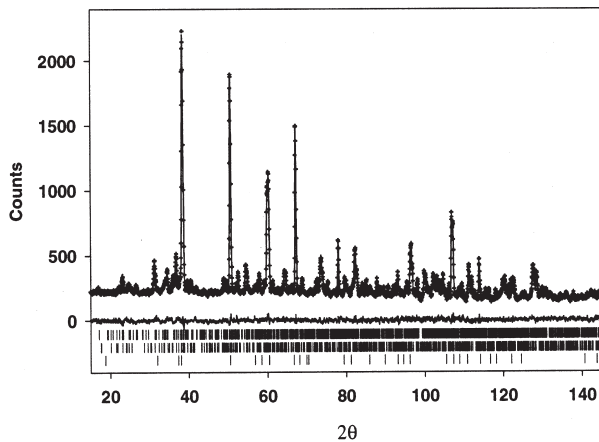
FIGURE 1. The observed (+), calculated and difference (solid lines) powder neutron diffraction profiles for hydroxyl-clinohumite. The middle and lower set of peak markers are those for hydroxyl-chondrodite and brucite, respectively.
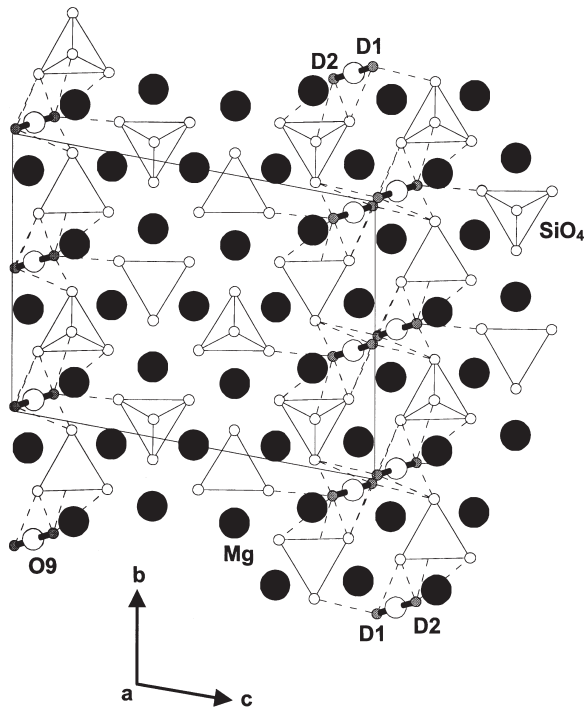

FIGURE 2. The structure of hydroxyl-clinohumite showing SiO$_4$ tetrahedra and the disordered D1 and D2 positions. The hydrogen bonds listed in Table 3 are indicated by dashed lines for the brucite-like layers.

FIGURE 3. Configuration of hydrogen positions in hydroxyl-clinohumite. The D1 and D2 positions associated with each O9 are shown although only the shaded position is occupied. The short D1-D1 distance is indicated by the dotted line.

Chakoumakos et al. 1997). The role of hydrogen bonding has also been inferred from the number and frequency of hydroxyl stretching vibrations (Ferraris et al. 2000).

Due to the constraints of the space group, two centrosymmetric D1 sites are present in close proximity [~1.01(2) Å] (Fig. 3). If both of these D1 sites were occupied there would be a significant destabilizing effect upon the structure. The presence of D1 and D2 positions in approximately equal proportions removes the necessity of a D1-D1 interaction. If a D1 position is occupied the nearest neighbor D1 site must be unoccupied and
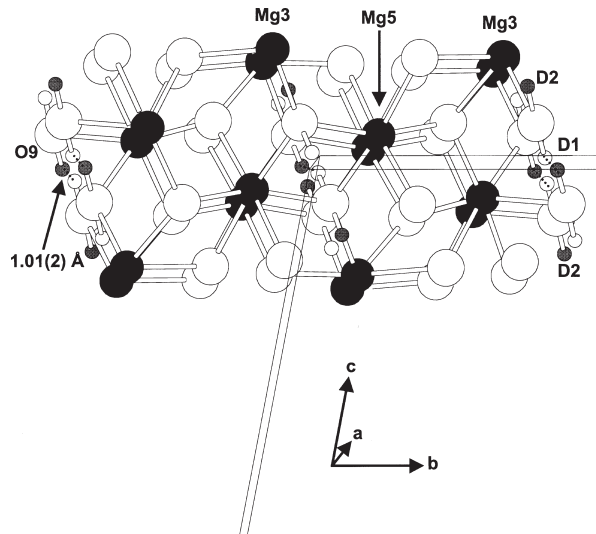
thus the associated O9 is bonded to a D2 atom.

The determination of H positions has been the focus of a number of studies using X-ray Fourier difference techniques. H1 and H2 sites have been observed in both hydroxyl-clinohumite (Ferraris et al. 2000) and hydroxyl-chondrodite (Yamamoto 1977). Fujino and Takéuchi (1978) on the other hand only noted H1-like sites in titanian chondrodite and titanian clinohumite containing Ti at almost 25% of the Mg5 sites. Similarly, only H1 positions were found for norbergite in which around 75% of the hydroxyl oxygen sites were occupied by F (Cámara 1997). In contrast, a series of energy calculations by Abbott et al. (1989) on hydroxyl, F, and Ti containing humite minerals found two energy minima corresponding to H1 and H2. They found that whereas the energies of the two sites were similar, H1 sites were favored only when an adjacent H2 site was occupied and that H2 positions were primary when F or Ti substitution had occurred. The present study confirms these calculations in the case of the hydroxyl end-member clinohumite; we are currently undertaking neutron diffraction studies of Ti and F substituted humite minerals.

The rarity of natural hydroxyl-humites has been attributed to the destabilizing effect of the expected H1-H1 interaction (Fujino and Takéuchi 1978; Cámara 1997). The substitution of F for OH [Mg$_7$Si$_4$O$_{14}$·2Mg$_2$(OH)$_{0.5}$F$_{0.5}$] and TiO$_2$ for Mg(OH)$_2$ [Mg$_7$Si$_4$O$_{14}$·2Mg$_{1.5}$Ti$_{0.5}$(OH)$_{0.5}$O$_{1.5}$] removes the possibility of this interaction, although the extent of the exchange is not always as great as required for apparent stabilization of the structure (Trommsdorff and Evans 1980; Ehlers and Hoinkes 1987; Okay 1994; Weiss 1997; Rahn and Bucher 1998). Further, hydroxyl-clinohumite with the simplified formula Mg$_7$Si$_4$O$_{14}$·2Mg$_2$(OH)$_{0.93}$F$_{0.07}$ has been reported recently (Ferraris et al. 2000). In agreement with this evidence of natural stability, this

work finds no crystal chemical reason for the hydroxyl-humites to be unstable under upper mantle conditions. Indeed, the experimentally determined stability field of synthetic hydroxyl-clinohumite (Yamamoto and Akimoto 1977; Burnley and Navrotsky 1996; Wunder 1998) indicates that it is stable to higher pressure and in particular higher temperature than titanian clinohumite (Merrill et al. 1972; Engi and Lindsley 1980; Weiss 1997). Instead, hydroxyl-clinohumite is rarely found in nature because of the favorable site available for Ti and F in clinohumite relative to other possible phases. This results in the concentration of these elements in clinohumite and inhibits the formation of the hydroxyl end-member in natural systems. The (Mg + Fe):Si ratio of hydroxyl-clinohumite is also inappropriate for typical mantle compositions. The absence of a crystal chemical instability in hydroxyl-clinohumite favors the possibility of clinohumite type defects as sites for water in mantle olivine since coupled incorporation of Ti or F is not required and appropriate compositions may be possible on a sub-grain scale.

ACKNOWLEDGMENTS

REFERENCES CITED

Abbott, 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 Akaogi, M. (1976) Titanochondrodite and titanoclinohumite derived from the upper mantle in the Buell Park kimberlite, Arizona, USA. Contributions to Mineralogy and Petrology, 56, 243–253.

Bell, D.R. and Rossman, G.R. (1992) Water in earth's mantle: The role of nominally anhydrous minerals. Science, 255, 1391–1397.

Burnley, P.C. and Navrotsky, A. (1996) Synthesis of high-pressure hydrous magnesium silicates: Observations and analysis. American Mineralogist, 81, 317–326.

Cámara, F. (1997) New data on the structure of norbergite: location of hydrogen by X-ray diffraction. Canadian Mineralogist, 35, 1523–1530.

Catti, M., Ferraris, G., Hull, S., and Pavese, A. (1995) Static compression and H disorder in brucite, Mg(OH)2, to 11 GPa: a powder neutron diffraction study. Physics and Chemistry of Minerals, 22, 200–206.

Chakoumakos, B.C., Loong, C-K., and Schultz, A.J. (1997) Low-temperature structure and dynamics of brucite. Journal of Physical Chemistry, 101, 9458–9462.

Ehlers, K. and Hoinkes, G. (1987) Titanian chondrodite and clinohumite in marbles from the Ötztal crystalline basement. Mineralogy and Petrology, 36, 13–25.

Engi, M. and Lindsley, D.H. (1980) Stability of titanium clinohumite: Experiments and thermodynamic analysis. Contributions to Mineralogy and Petrology, 72, 415–424.

Ferraris, G., Prencipe, M., Sokolova, E.V., Gekimyants, V.M., and Spiridonov, E.M. (2000) Hydroxylclinohumite, a new member of the humite group: twinning, crystal structure and crystal chemistry of the clinohumite subgroup. Zeitschrift für Kristallographie, 215, 169–173.

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

Howard, C.J. and Hunter, B.A. (1997) A computer program for Rietveld analysis of X-ray and neutron powder diffraction patterns (Australian Nuclear Science and Technology Organisation, Menai).

Kitamura, M., Kondoh, S., Morimoto, N., Miller, G.H., Rossman, G.R., and Putnis, A. (1987) Planar OH-bearing defects in mantle olivine. Nature, 328, 143–145.

Kohlstedt, D.L., Keppler, H., and Rubie, D.C. (1996) Solubility of water in the α, β and γ phases of (Mg, Fe)$_2$SiO$_4$. Contributions to Mineralogy and Petrology, 123, 345–357.

McGetchin, T.R., Silver, L.T., and Chodos, A.A. (1970) Titanoclinohumite: A possible mineralogical site for water in the upper mantle. Journal of Geophysical Research, 75, 255–259.

Merrill, R.B., Robertson, J.K., and Wyllie, P.J. (1972) Dehydration reaction of titanoclinohumite: Reconnaissance to 30 kilobars. Earth and Planetary Science Letters, 14, 259–262.

Okay, A.I. (1994) Sapphirine and Ti-clinohumite in ultra-high-pressure garnet-pyroxenite and eclogite from Dabie Shan, China. Contributions to Mineralogy and Petrology, 116, 145–155.

Rahn, M.K. and Bucher, K. (1998) Titanian clinohumite formation in the Zermatt-Saas ophiolites, central Alps. Mineralogy and Petrology, 64, 1–13.

Rietveld, H.M. (1969) A profile refinement method for nuclear and magnetic structures. Journal of Applied Crystallography, 2, 65–71.

Robinson, K., Gibbs, G.V., and Ribbe, P.H. (1973) The crystal structures of the humite minerals. IV. clinohumite and titanoclinohumite. American Mineralogist, 58, 43–49.

Trommsdorff, V. and Evans, B.W. (1980) Titanian hydroxyl-clinohumite: Formation and breakdown in antigorite rocks (Malenco, Italy). Contributions to Mineralogy and Petrology, 72, 229–242.

Weiss, M. (1997) Clinohumites: A field and experimental study. Ph.D. thesis No. 12202, Swiss Federal Institute of Technology Zurich.

Woodland, A.B. and O'Neill, H.St.C. (1997) Thermodynamic data for Fe-bearing phases obtained using noble metal alloys as redox sensors. Geochimica et Cosmochimica Acta, 61, 4359–4366.

Wunder, B. (1998) Equilibrium experiments in the system MgO-SiO$_2$-H$_2$O (MSH): stability fields of clinohumite-OH [Mg$_9$Si$_4$O$_{16}$(OH)$_2$], chondrodite-OH [Mg$_5$Si$_2$O$_8$(OH)$_2$] and phase A (Mg$_7$Si$_2$O$_8$(OH)$_6$). Contributions to Mineralogy and Petrology, 132, 111–120.

Yamamoto, K. (1977) The crystal structure of hydroxyl-chondrodite. Acta Crystallographica, B33, 1481–1485.

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