American Mineralogist, Volume 86, pages 176–180, 2001

O-D···O bond geometry in OD-chondrodite

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ABSTRACT

The crystal structure of OD-chondrodite [$Mg_5Si_2O_8(OD)_2$, $P2_1/b$ (a unique), a = 4.74711(5), b = 10.34888(16), c = 7.90228(13) Å, α = 108.678(1)°] was refined to wR_p = 0.0218, χ^2 = 3.545 at ambient conditions using time-of-flight neutron powder data. The disordered H model proposed for OH-chondrodite on the basis of single-crystal X-ray data is confirmed. The occupations of the D1 and D2 sites are, respectively, 0.52(1) and 0.48(1). The long O5-D1 [1.076(4) Å] and O5-D2 [1.111(4) Å] bond lengths, which are two of the longest O-H(D) bonds observed in mineral structures, reflect the positional disorder of the O5 atom in the unshared OH-OH edge. Both D1 [1.968(4), 2.489(4) Å] and D2 [2.149(4), 2.251(4) Å] atoms are involved in two hydrogen bonds. A re-examination of the origin of positive OH frequency shifts in both F-bearing and OH-chondrodite at high pressure is warranted in view of the crystallographic data.

INTRODUCTION

The most significant work on the crystal chemistry of humites occurred over a ten-year period beginning about 1968. Initial studies focussed primarily on the chemistry and crystallographic nomenclature (Ribbe et al. 1968; Jones et al. 1969; Jones 1969). This was followed by a series of single-crystal X-ray refinements of the structures of norbergite (Gibbs and Ribbe 1969), chondrodite (Gibbs et al. 1970), humite (Ribbe and Gibbs 1971), clinohumite and titanian clinohumite (Robinson et al. 1973; Kocman and Rucklidge 1973; Fujino and Takéuchi 1978), and OH-chondrodite (Yamamoto 1977). More recently, single-crystal X-ray refinements have been reported for norbergite (Cámara 1997) and a natural hydroxylclinohumite (Ferraris et al. 2000). The crystal structure of titanian clinohumite has also been refined using single-crystal neutron diffraction data (Smyth et al. 1994).

The humites can be represented by the general formula, $n[Mg_2SiO_4]\cdot[M_{1-x}Ti_x(F,OH)_{2-2x}O_{2x}]$, where M is primarily Mg with minor amounts of Fe^{2+}, Mn, Ni, Ca, Zn, Cu, $0 \leq x \leq 0.5$ and n = 1, 2, 3, and 4 for norbergite, chondrodite, humite, and clinohumite, respectively. The [O, (OH,F)] atoms are arranged in hexagonal closest packed arrays with M and Si cations occupying the octahedral (50%) and tetrahedral (8–12% for n = 1–4) sites (Ribbe 1980). The (F,OH,O) anion is triangularly coordinated to three M cations. In terms of a polyhedral model, the structures consist of chains of edge-sharing octahedra linked by silicate tetrahedra. The positions of the H atoms have been determined for OH-chondrodite (Yamamoto 1977), titanian clinohumite (Fujino and Takéuchi 1978; Smyth et al. 1994), norbergite (Cámara 1997), and hydroxylclinohumite (Ferraris et al. 2000). Structure-energy calculations have also been used to locate H-atom positions in several humite minerals, including OH-chondrodite and titanian clinohumite (Abbott et al. 1989).

Experimental work in the MgO-SiO_2-H_2O (MSH) system has shown that both OH-clinohumite and OH-chondrodite are stable at P-T conditions (700–1100 °C and 2.9–7.7 GPa) representative of the upper mantle (Yamamoto and Akimoto 1977; Akaogi and Akimoto 1980). More recent investigations in both the MSH system, and natural or synthetic systems that mimic the composition of typical mantle rock, have extended the stability range of both OH end-members to approximately 14 GPa at 1100 °C (Khodyrev et al. 1992; Kawamoto et al. 1995; Luth 1995; Burnley and Navrotsky 1996; Wunder 1998).

In recent years, there has been a resurgence of interest in chondrodite and clinohumite among spectroscopists who have investigated elastic properties (Beckman Fritzel and Bass 1997; Sinogeikin and Bass 1999) and the pressure and/or temperature dependence of OH vibrational frequencies (Williams 1992; Lin et al. 1999; Hofmeister et al. 1999; Mernagh et al. 1999; Lin et al. 2000). Spectroscopic methods have also been used to probe the nature of the H-atom environment in both natural F-bearing chondrodite and synthetic OH-chondrodite and OH-clinohumite (Akaogi and Akimoto 1986; Cynn et al. 1996; Phillips et al. 1997). Bulk moduli determined from diffraction data have been reported for F-bearing chondrodite (Faust and Knittle 1994; Kuribayashi et al. 1998; Friedrich et al. 2000)

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0003-004X/01/0102–176$05.00

and OH-chondrodite and OH-clinohumite (Ross and Crichton 1999; Lager et al. 1999).

Although OH is known to effect the stability and physical properties of humites, no neutron diffraction data on the O-H···O bond have been reported for any of the OH end-members of the humite group. In this study, the crystal structure of OD-chondrodite has been refined using time-of-flight (TOF) neutron powder data.

EXPERIMENTAL METHODS

The sample (300 mg) was synthesized from gels in five experimental runs (24–96 h) using an end-loaded piston-cylinder apparatus (850 °C, 3.6 GPa) and a Walker-type multi-anvil press (900 °C, 5.0 GPa). The H_2O-free $5MgO{\cdot}2SiO_2$ gel used as starting material was produced from stoichiometric amounts of magnesium nitrate-tetrahydrate (>99.8%, Alpha Products) and tetraethyloxysilane (>99% Fluka) following the method described by Hamilton and Henderson (1968). In all experiments, 12–14 wt% excess D_2O was added to the gel which was then sealed in gold capsules with outer diameters of 3.0 and 4.0 mm. Piston-cylinder runs were carried out using NaCl-Pyrex-MgO assemblies. MgO-octahedra assemblies (19 mm) and WC anvils with 12 mm truncation-edge lengths were used in the multi-anvil experiments. All solid run products, as examined by X-ray powder diffraction and Raman microspectroscopy, contained minor amounts of brucite $Mg(OD)_2$ in addition to OD-chondrodite.

TOF neutron powder data were collected at ambient conditions for 15 h using the POLARIS diffractometer at the U.K. pulsed neutron source, ISIS. The POLARIS instrument is a high-intensity, medium-resolution ($\Delta d/d$ = ~0.5, 0.7, and 1% at 2θ = 145°, 90°, and 35°, respectively) diffractometer with a flight path of 12 m (Hull et al. 1992).

Data reduction and Rietveld refinement were carried out using the General Structure Analysis System (GSAS) (Larson and Von Dreele 1994). Data from three detector banks were refined simultaneously (145°, 90°, and 35°). The *d*-spacing ranges and the number of reflections generated for each histogram were 0.5–3.2 (3551), 0.5–4.0 (3770), and 0.8–5.6 Å (983) for the 145°, 90°, and 35° banks, respectively. Peak shapes for each of the phases were fitted with TOF profile function 3 in GSAS. The dominant Gaussian and Lorentzian lineshape parameters (σ_1 and γ_1) in this function were varied during refinement. A cosine Fourier series was used to fit the background for each of the diffraction profiles. Starting parameters in the refinement were taken from Yamamoto (1977). The structure was refined in the non-standard space group $P2_1/b$ (*a* unique) to facilitate comparison with olivine. Unit-cell parameters [a = 4.74711(5), b = 10.34888(16), c = 7.90228(13) Å, α = 108.678(1)°] were in good agreement with those reported by Yamamoto (1977). Due to the complexity of the structure, anisotropic displacement parameters were varied only for O5, D1, and D2. The site occupancy factors for D1 and D2 were determined by alternately refining the occupancy and displacement parameters until convergence was achieved. The sample contained ~6 wt% brucite based on refinement of the phase fraction. The final discrepancy factor was $wR_p = 0.0218$ with $\chi^2 = 3.545$ for 117 variables. Final refinement profiles are shown in Figure 1. Atom parameters, anisotropic displacement

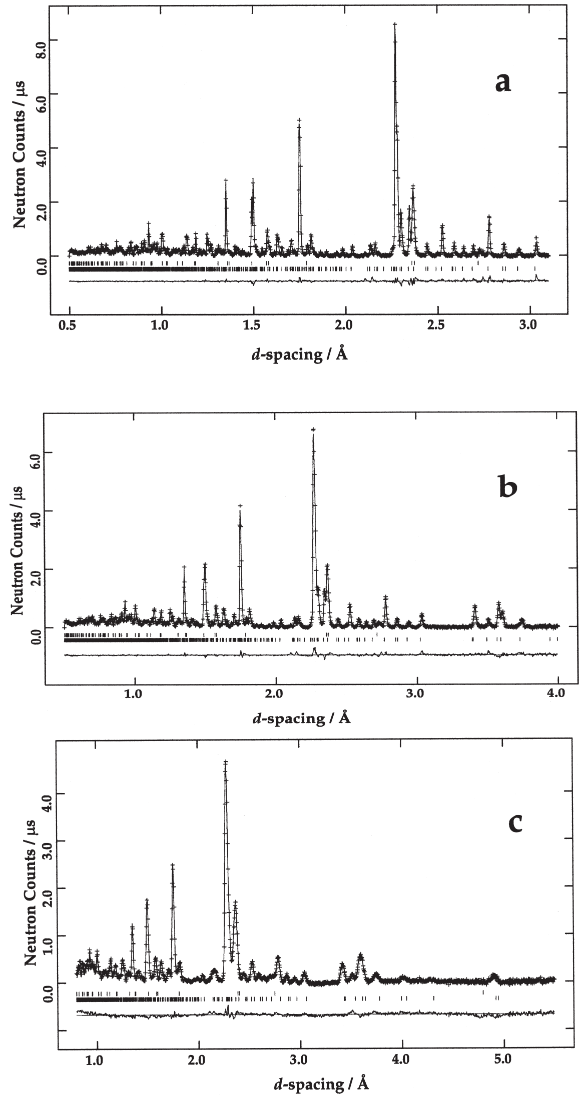

FIGURE 1. Refinement profiles for the 145° (**a**), 90° (**b**), and 35° (**c**) detector banks. Plus signs represent the observed data. Solid line is the least-squares fit. Tick marks below the profile indicate the position of all allowed Bragg reflections for brucite (top) and chondrodite. Background was fitted as part of the refinement but subtracted before plotting.

TABLE 1. Atom fractional coordinates and isotropic displacement factors (×100)

Atom	*x*	*y*	*z*	*U* or U_{eq}(Å^2)*
Mg1	0.5	0.0	0.5	0.62(3)
Mg2	0.0076(4)	0.1753(1)	0.3079(2)	0.58(3)
Mg3	0.4887(3)	0.8836(1)	0.0770(2)	0.57(2)
Si	0.0791(2)	0.1409(2)	0.7021(2)	0.30(2)
O1	0.7743(3)	0.0030(1)	0.2953(2)	0.57(2)
O2	0.7276(3)	0.2438(1)	0.1287(2)	0.49(2)
O3	0.2244(3)	0.1683(1)	0.5288(2)	0.67(2)
O4	0.2620(3)	0.8564(1)	0.2968(2)	0.64(2)
O5	0.2628(3)	0.0600(2)	0.1048(2)	1.23(3)
D1	0.0886(7)	0.0192(4)	0.0168(5)	4.67(5)
D2	0.4339(7)	0.1002(4)	0.2035(5)	3.85(5)

*U_{eq} for O5, D1, and D2 was computed according to the formula $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*a_ia_j$.

TABLE 2. Anisotropic displacement parameters (×100) for O5, D1, and D2 atoms

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O5	1.38(6)	0.91(5)	1.37(7)	0.60(5)	0.96(5)	0.37(5)
D1	4.8(2)	3.0(2)	5.2(2)	–0.2(2)	–3.2(2)	–0.2(1)
D2	3.2(2)	4.8(2)	3.0(2)	–0.1(2)	–0.8(2)	0.5(2)

parameters and interatomic distances and angles are given in Tables 1–3.

RESULTS AND DISCUSSION

An important feature of the OD(H)-chondrodite structure is the relatively short, unshared OH-OH edge, i.e., O5···O5 (Fig. 2 and Table 3). In space group $P2_1/b$, adjacent anion sites (O5/OH) in the unshared edge are related by a center of symmetry. Based on the X-ray model, H atoms are statistically distributed over two sites (50% occupancy), i.e., different H sites are occupied on adjacent OH groups (Yamamoto 1977). For example, if an H1 site is occupied on one OH, then H2 would be occupied on the adjacent OH, and vice versa. In this model, O-H vectors are located to one side or the other of adjacent O5 atoms and would point in the same direction. Short H-H distances are avoided because the H sites are only half occupied.

The occupations of the D1 and D2 sites in OD-chondrodite are equivalent within experimental uncertainty [0.52(1) and 0.48(1), respectively], confirming the X-ray results described above. The O-D bonds [O5-D1 = 1.076(4) Å, and O5-D2 = 1.111(4) Å] are two of the longest O-D(H) distances observed in mineral structures (Table 3). The two O5-D vectors are aligned along almost opposing directions as indicated by the nearly straight D1-O5-D2 angle [175.8(4)°]. The long O5-D distances are consistent with the apparent displacement ellipsoid of O5, which is elongated parallel to the O-D vectors (Fig. 3). The O5 atom is most likely statically (spatially) disordered and occupies two positions corresponding to the two types of D sites. Because bond distances reflect mean atomic positions, both O-D distances would be lengthened relative to the values observed in an ordered arrangement.

The O disorder reflects the local structural environment of D(H), which is significantly different for D1 and D2 sites (Fig. 3). D1 is involved in one nearly straight [1.968(4) Å; ∠O5-D1···O5 = 169.4(4)°] and one very bent [2.489(4) Å; ∠O5-D1···O1 = 81.31(4)°] hydrogen bond (Table 3). Hydrogen bridges for D2 are approximately of the same length [2.149(4) and 2.251(4) Å], and both are involved in narrow O-D···O angles [132.6(4) and 113.5(4)°, respectively].

TABLE 3. Selected interatomic distances (Å) and angles (°)

Mg1-O1 [2]	2.085(1)	Oh5-D1	1.076(4)
Mg1-O3 [2]	2.132(1)	D1···O1	2.489(2)
Mg1-O4 [2]	2.130(2)	D1···O5	1.968(4)
		O1···O5	2.926(4)
Mg2-O1	2.074(2)	O5···O5	3.031(2)
Mg2-O2	2.218(2)		
Mg2-O3	2.048(2)	O5-D1···O1	81.34(4)
Mg2-O3	2.180(2)	O5-D1···O5	169.4(4)
Mg2-O4	2.195(2)	D1-O5-D2	175.8(4)
Mg2-O5	2.059(2)		
		O5-D2	1.111(4)
Mg3-O1	2.231(2)	D2···O2	2.251(3)
Mg3-O2	2.015(2)	D2···O1	2.149(4)
Mg3-O2	2.110(2)		
Mg3-O4	2.137(2)	O5-D2···O1	132.6(4)
Mg3-O5	2.067(2)	O5-D2···O2	113.5(4)
Mg3-O5	2.082(2)		
Si-O1	1.650(2)		
Si-O2	1.640(2)		
Si-O3	1.638(2)		
Si-O4	1.619(2)		

As expected, the maximum root-mean-square displacement of both D1 and D2 is oriented perpendicular to the O-D bond. The greater anisotropy of the D1 atom is related, in part, to the geometry of the O5-D1···O5 bond [∠O5-D1···O5 = 169.4(4)°], which constrains the displacement parallel to the bond axis (Fig. 3).

Spectroscopic studies of chondrodites at high pressure

Williams (1992) has collected IR spectra for a natural F-bearing chondrodite to pressures in excess of 40 GPa. One important conclusion from this study is that two of the three OH vibrations in chondrodite shift to higher frequencies with pressure. If hydrogen bonding increases with pressure due to compression of the O-O distances, one would expect a shift in the opposite direction, i.e., to lower frequencies, based on the relationships derived from hydrogen bonded systems at ambient pressure. This behavior has been well documented in several hydrous minerals, e.g., $Mg(OH)_2$ (Kruger et al. 1989) and kaolinite and aluminous serpentine (Velde and Martinez 1981). Williams proposes that these "anomalous" positive frequency shifts in chondrodite may be due to H-H repulsions which be-

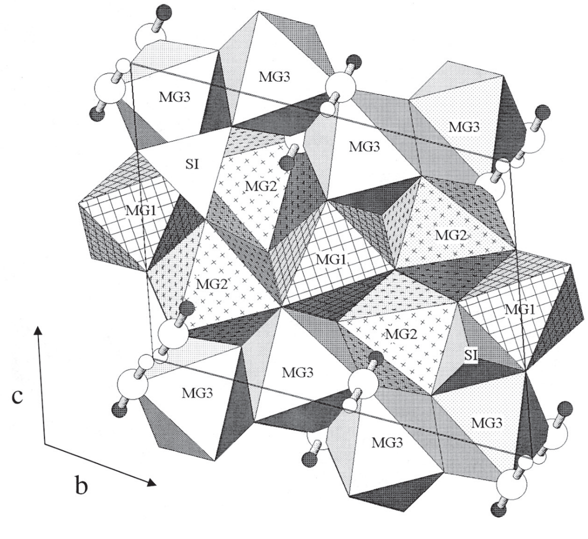

FIGURE 2. [100] projection of the unit cell of the OD(H)-chondrodite structure at ambient conditions (ATOMS, V5.06, Shape Software). D1 and D2 atoms are represented by the small white and dark spheres, respectively. The larger sphere represents the O5 atom. An unshared OD-OD edge is shown at the origin of the unit cell.

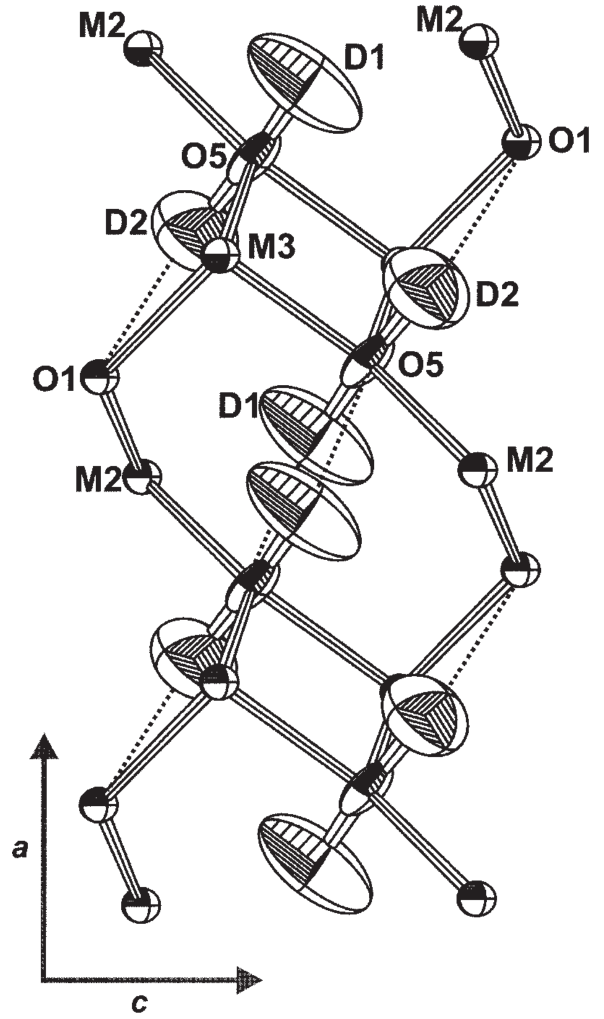

FIGURE 3. [010] projection of part of the OD-chondrodite structure showing the D-atom environment (ATOMS, V5.06, Shape Software). The short hydrogen bonds involving D1 and D2 are represented by dashed lines. The unshared OD-OD edge is shown at the center of the drawing. Ellipsoids are drawn for 99% probability.

come more pronounced at high pressure and act to destabilize the structure. A similar argument has been used to explain the positive frequency shift in the IR spectra of hydrogarnet (Knittle et al. 1992).

Lin et al. (1999) have collected ambient and high-pressure Raman data for OH-chondrodite and a natural F-bearing phase. The frequencies of all Raman bands in both phases increase with pressure. In the case of OH-chondrodite, Lin et al. (1999) proposed that H-H repulsion will be the most significant contributor to the positive frequency shifts associated with both the symmetric and the asymmetric O-H stretching vibrations. The positive shifts observed in F-bearing chondrodite were attributed to a lengthening of hydrogen bonds.

Several of the conclusions in the above studies are based on an incorrect interpretation of the crystallographic data. For example, in the F-bearing chondrodite investigated by Williams (1992), only about one-quarter of the O5 sites are protonated in the unshared OH-OH edge (~25% occupancy of H1 sites) (Fig. 3). There are no unrealistically, short H-H distances (and H-H repulsions) because the center of symmetry is violated in the local structural environment, i.e., OH is adjacent to F and not another OH. Williams (1992) also assigned the absorption bands in F-bearing chondrodite based on the existence of two OH sites, one associated with the M3 site and the other with the M2 site. If OH ≤ 1 atom per formula unit, there is only one OH site that is coordinated to both M3 and M2. This invalidates the argument by Williams (1992) that significant hydrogen bonding is associated with the M2 site but not with the M3 site.

The interpretation of the Raman data presented by Lin et al. (1999) for OH-chondrodite is based on a compression mechanism that involves H-H repulsion between adjacent OH groups. When H is disordered, H atoms cannot be in close proximity because different H sites are occupied on adjacent OH groups. Therefore, it is difficult to understand why strong H-H repulsions develop between OH groups at high pressure.

Cynn and Hofmeister (1994) and Hofmeister et al. (1999) have suggested an alternate explanation for the positive frequency shifts in dense, hydrous magnesium silicates. They found a good correlation between the frequency (ν) of the OH band at ambient pressure and the change in frequency at high pressure ($d\nu/dp$) (refer to Fig. 12, Hofmeister et al. 1999). High-frequency bands, which reflect weak hydrogen bonding, should show positive pressure shifts related to O-H bond compression. The argument is that the O atom in the hydrogen bond is simply too far away so that the O-H bond behaves as a normal metal-oxygen bond during compression. Notable exceptions to this behavior are hydrogarnet, and simple metal hydroxides, structures in which H-H repulsions may also be important (Knittle et al. 1992; Lager and Von Dreele 1996; Parise et al. 1994, 1999). Stronger hydrogen bonding and lower frequencies result in negative shifts because the hydrogen bond strength increases significantly as O-O distances compress.

Based on the model proposed by Hofmeister et al. (1999), the positive pressure dependence ($+d\nu/dp$) of O-H bands in F-bearing [O···O = 2.939(1) Å; O···H = 1.918 (4) Å; Friedrich et al., in preparation] and OH-chondrodite (Table 3) is consistent with the existence of weak hydrogen bonds in these structures. The frequency shifts could also be related to bending of the O-H···O bond angle, as discussed by Hofmeister et al. (1999) for phase B, $Mg_{12}{}^{VI}Si^{IV}Si_3O_{19}(OH)_2$. For example, a weakening of hydrogen bonds, and a corresponding decrease in the O-H···O angle, could occur if O-H vectors rotate away from the O atom into vacant polyhedral sites at high pressure.

A re-examination of the origin of the positive frequency shifts in both F-bearing and OH-chondrodite is warranted in view of the crystallographic data. However, it will likely require accurate information on the pressure dependence of the H-atom positions, which is currently not available.

ACKNOWLEDGMENTS

Travel for G.A.L. to the ISIS pulsed neutron source was supported by a research grant from the Arts and Sciences College at the University of Louisville. This work was also supported in part by NSF grant EAR-0073734 to G.A.L. Comments by Bryan Chakoumakos, Anne Hofmeister, and two anonymous reviewers significantly improved the manuscript.

REFERENCES CITED

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

Akaogi, M. and Akimoto, S.-I. (1980) High-pressure stability of a dense hydrous magnesian silicate $Mg_{23}Si_8O_{42}H_6$ and some geophysical implications. Journal of Geophysical Research, 85, B12, 6944–6948.

———(1986) Infrared spectra of high-pressure hydrous silicates in the system MgO-SiO_2-H_2O. Physics and Chemistry of Minerals, 13, 161–164.

Beckman Fritzel, T.L. and Bass, J.D. (1997) Sound velocities of clinohumite, and implications for water in the Earth's mantle. Geophysical Research Letters, 24, 1023–1026.

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.

Cynn, H. and Hofmeister, A.M. (1994) High-pressure IR spectra of lattice modes and OH vibrations in Fe-bearing wadsleyite. Journal of Geophysical Research, 99, 17,717–17,727.

Cynn, H., Hofmeister, A.M., Burnley, P.C., and Navrotsky, A. (1996) Thermodynamic properties and hydrogen speciation from vibrational spectra of dense hydrous magnesium silicates. Physics and Chemistry of Minerals, 23, 361–376.

Faust, J. and Knittle, E. (1994) Static compression of chondrodite: Implications for water in the upper mantle. Geophysical Research Letters, 21, 1935–1938.

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.

Friedrich, A., Kunz, M., Miletich, R., and Lager, G.A. (2000) Compressibility of chondrodite, $Mg_5(SiO_4)_2(OH,F)_2$ up to 9.6 GPa: The effect of F/OH substitution on the bulk modulus. EMPG-8, Bergamo, Italy, April 2000.

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

Gibbs, G.V. and Ribbe, P.H. (1969) The crystal structures of the humite minerals. I. Norbergite. American Mineralogist, 54, 376–390.

Gibbs, G.V. Ribbe, P.H., and Anderson, C.P. (1970) The crystal structures of the humite minerals. II. Chondrodite. American Mineralogist, 55, 1182–1194.

Hamilton, D.L. and Henderson C.M.B. (1968) The preparation of silicate compositions by a gelling method. Mineralogical Magazine, 36, 832–838.

Hofmeister, A.M., Cynn, H., Burnley, P.C., and Meade, C. (1999) Vibrational spectra of dense, hydrous magnesium silicates at high pressure: Importance of the hydrogen bond angle. American Mineralogist, 84, 454–464.

Hull, S., Smith, R.I., David, W.I.F., Hannon, A.C., Mayers, J., and Cywinski, R. (1992) The POLARIS Powder Diffractometer at ISIS. Physica B, 180 and 181, 1000–1002.

Jones, N.W. (1969) Crystallographic nomenclature and twinning in the humite minerals. American Mineralogist, 54, 309–313.

Jones, N.W., Ribbe, P.H., and Gibbs, G.V. (1969) Crystal chemistry of the humite minerals. American Mineralogist, 54, 391–411.

Kawamoto, T., Leinenweber, K., Hervig, R.L., and Holloway, J.R. (1995) Stability of hydrous minerals in H_2O-saturated KLB-1 peridotite up to 15 GPa. In K.A Farley, Ed., Volatiles in the Earth and Solar System, p. 229–239. American Institute of Physics, College Park, Maryland.

Khodyrev, O.Y., Agoshkov, V.M., and Slutsky, A.B. (1992) The system peridotite-aqueous fluid at upper mantle parameters. Transactions of the USSR Academy of Science: Earth Science Section, 312, 255–258.

Knittle, E., Hathorne, A., Davis, M., and Williams, Q. (1992) A spectroscopic study of the high-pressure behavior of the O_4H_4 substitution in garnet. In Y. Syono and M. Manghnani, Eds., High-Pressure Research: Applications to Earth and Planetary Sciences, p. 297–304. Terra Publishing Company, Tokyo.

Kocman, V. and Rucklidge, J. (1973) The crystal structure of titaniferous clinohumite. Canadian Mineralogist, 12, 39–45.

Kruger, M.B., Williams, Q., and Jeanloz, R. (1989) Vibrational spectra of $Mg(OH)_2$ and $Ca(OH)_2$ under pressure. Journal of Chemical Physics, 91, 5910–5915.

Kuribayashi, T., Kudoh, Y., and Akizuki, M. (1998) Single-crystal X-ray diffraction and FT- IR spectra of chondrodite, $Mg_5Si_2O_8(OH,F)_2$ under high pressure to 6.0 GPa. 17th General Meeting of the International Mineralogical Association, Toronto, A44.

Lager, G.A. and Von Dreele, R.B. (1996) Neutron powder diffraction study of hydrogarnet to 9.0 GPa. American Mineralogist, 81, 1097–1104.

Lager, G.A., Ulmer, P., Miletich, R. and Marshall, W.G. (1999) Crystal structure and static compression of OD-chondrodite. EOS, Transactions of the American Geophysical Union, 80, F1139.

Larson, A.C. and Von Dreele, R.B. (1994) General Structure Analysis System (GSAS). Los Alamos National Laboratory Report LAUR 86-748.

Lin, C.C., Liu, L.-G., and Irifune, T. (1999) High-pressure Raman spectroscopic study of chondrodite. Physics and Chemistry of Minerals, 26, 226–233.

Lin, C.C., Liu, L.-G., Mernagh, T.P., and Irifune, T. (2000) Raman spectroscopic study of hydroxyl-clinohumite at various temperatures and pressures. Physics and Chemistry of Minerals, 27, 329–331.

Luth, R.W. (1995) Is phase A relevant to the earth's mantle? Geochimica et Cosmochimica Acta, 59, 679–682.

Mernagh, T.P., Liu, L.G., and Lin, C.C. (1999) Raman spectra of chondrodite at various temperatures. Journal of Raman Spectroscopy, 30, 963–969.

Parise, J.B., Leinenweber, K., Weidner, D.J., Tan, K., and Von Dreele, R.B. (1994) Pressure induced H bonding: neutron diffraction study of brucite, $Mg(OD)_2$, to 9.3 GPa. American Mineralogist, 79, 193-196.

Parise, J.B., Loveday, J.S., Nelmes, R.J., and Kagi, H. (1999) Hydrogen repulsion "transition" in $Co(OD)_2$ at high pressure? Physical Review Letters, 83, 328-331.

Phillips, B.L., Burnley, P.C., Worminghaus, K., and Navrotsky, A. (1997) ^{29}Si and ^1H NMR spectroscopy of high-pressure hydrous magnesium silicates. Physics and Chemistry of Minerals, 24, 179–190.

Ribbe, P.H. (1980) The humite series and Mn-analogs. In P.H. Ribbe, Ed., Orthosilicates, 5, 231–274. Mineralogical Society of America Reviews in Mineralogy, Washington, D.C.

Ribbe, P.H. and Gibbs, G.V. (1971) Crystal structures of the humite minerals: III. Mg/Fe ordering in humite and its relation to other ferromagnesian silicates. American Mineralogist, 56, 1155–1173.

Ribbe, P.H., Gibbs, G.V., and Jones, N.W. (1968) Cation and anion substitutions in the humite minerals. Mineralogical Magazine, 37, 966–975.

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.

Ross, N.L. and Crichton, W. (1999) Compressibility of OH-clinohumite and OH-chondrodite. American Geophysical Union Meeting, San Francisco, December 1999.

Sinogeikin, S.V. and Bass, J.D. (1999) Single-crystal elastic properties of chondrodite: implications for water in the upper mantle. Physics and Chemistry of Minerals, 26, 297–303.

Smyth, J.R., Swope, R.J., and Larson, A.C. (1994) Crystal chemistry of H in clinohumite. EOS, Transactions of the American Geophysical Union, 75, 231–232.

Velde, B. and Martinez, G. (1981) Effect of pressure on OH stretching frequencies in kaolinite and aluminous serpentine. American Mineralogist, 66, 196–200.

Williams, Q. (1992) A vibrational spectroscopic study of hydrogen in high pressure mineral assemblages. In Y. Syono and M. Manghnani, Eds., High-Pressure Research: Applications to Earth and Planetary Sciences, p. 289–296. Terra Publishing Company, Tokyo.

Wunder, B. (1998) Equilibrium experiments in the system MgO-SiO_2-H_2O (MSH): stability fields of clinohumite-OH [$Mg_9Si_4O_{16}(OH)_2$], chondrodite-OH [$Mg_5Si_2O_8(OH)_2$] and phase A [$Mg_7Si_2O_8(OH)_6$]. 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_2O 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 MARCH 7, 2000
MANUSCRIPT ACCEPTED AUGUST 30, 2000
PAPER HANDLED BY BRYAN CHAKOUMAKOS