Elastic Properties of Hydrogrossular Garnet and Implications for Water in the Upper Mantle

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The single-crystal elastic properties of a hydrous silicate garnet, hibschite $(Ca_3Al_2(SiO_4)_{1.72}(H_4O_4)_{1.28})$, were measured using Brillouin spectroscopic techniques. The adiabatic bulk modulus of hibschite, $K_S = 99.8\pm1.0$ GPa, and the shear modulus, $\mu = 64.3\pm0.5$ GPa, are 40% lower than the bulk and shear moduli for anhydrous grossular garnet $Ca_3Al_2(SiO_4)_3$. This increased compressibility of hydrogarnet is attributed to increased hydrogen bonding with pressure in the H_4O_4 tetrahedron. Density considerations indicate that hydrogarnet is likely to be stable relative to an assemblage with H_2O as a separate phase throughout the upper mantle and probably the transition zone. Assuming garnet to be the sole repository for mantle water, the seismic wave velocities of a "wet" eclogitic layer are 6-8% lower than those of dry eclogite. A hydrated eclogitic layer several times thicker than the oceanic crust would probably be required for a water-rich region of the mantle to be seismologically detectable. Lesser quantities of mantle water than those implied by the above scenario may be invisible to seismic techniques.

INTRODUCTION

Throughout the evolution of the Earth it is possible that water has been stored in the interior so that at present there may be, inside our planet, several times the amount of water as is in the hydrosphere [*Ahrens*, 1989]. Where and in what form this water may be stored in the mantle are questions which may be answered by examining hydrous phases transported from the mantle [*Bell and Rossman*, 1992a] and by considering the phase relations and properties of high-pressure hydrous phases [*Thompson*, 1992]. Among the candidate "wet" mantle phases synthetic phase B has attracted attention because of its high density and the fact that it is stable to pressures characteristic of the transition zone [*Ringwood and Major*, 1967; *Akaogi and Akimoto*, 1980]. However, as pointed out by *Finger et al.* [1989], phase B has not yet been demonstrated to be a stable phase for a likely bulk mantle composition. In addition to the high-pressure hydrous phases which have been synthesized, some naturally occurring upper mantle minerals such as olivine and pyroxene are able to incorporate OH and are potential storage sites for water [*Bell and Rossman*, 1992a]. Serpentine has been shown to remain hydrated up to 25 GPa and 900 K [*Meade and Jeanloz*, 1991]. Another mineral which is both petrologically relevant to the upper mantle and transition zone, and which has a hydrated form, is garnet. *Aines and Rossman* [1984] and *Bell and Rossman* [1992b] have investigated the OH content of mantle-derived garnets and have found hydrous components of 50-100 ppm (as H_2O) in

pyralspites, while in ugrandites it may range up to 20 wt % H_2O [*Rossman and Aines, 1991; Lager et al.*, 1989]. Some natural hydrogarnets are estimated to have equilibrated at pressures of as much as ~6 GPa (~180-km depth) and temperatures to ~1300°C. Additionally, hydrous garnets have been synthesized at temperatures of 800-1200°C and pressures of 2-5 GPa [*Ackermann et al.*, 1983; *Geiger et al.*, 1991]. Therefore, because garnet is a substantial fraction of the upper mantle, the potential of this phase as a water-bearing component of the Earth's interior warrants investigation. Garnet is also relevant because of the possibility that the OH contained in a variety of mantle silicates is incorporated via the hydrogarnet substitution, $H_4O_4 = SiO_4$.

It has previously been argued that because the molar volume increases with hydrogarnet substitution (~20% at zero pressure), garnet would not be a favorable phase to hold water at high pressures [*Martin and Donnay*, 1972]. *Aines and Rossman* [1984] suggested, however, that if hydrogarnet is more compressible than pure silicate (anhydrous) garnet, it could exist as a hydrous mantle component. To address the question of hydrogarnet compressibility we have used Brillouin spectroscopy to determine the elastic properties of a single crystal of hydrogrossular garnet at ambient conditions. Although pyrope, the magnesium end-member, may be a more abundant garnet component in the upper mantle, we chose to examine a Ca-rich garnet because much more OH can be incorporated into calcic garnets: there is, in fact, complete solid solution between the anhydrous end-member $Ca_3Al_2Si_3O_{12}$ (grossular) and a hydrous silica-free end-member, $Ca_3Al_2(H_4O_4)_3$ (synthetic phase). By using samples in this system, it should be possible to clearly identify the effect of the $H_4O_4 = SiO_4$ substitution on the elastic properties of garnets.

The hydrogrossular series is described by the formula $Ca_3Al_2(SiO_4)_{3-x}(H_4O_4)_x$. Hibschite is the mineralogical name for garnets with $0<x<1.5$, while for $1.5<x = 3.0$ the garnet is known as katoite [*Passaglia and Rinaldi*, 1984]. A natural hibschite, with ~57% grossular component ($x = 1.28\pm.08$), was used in our study so that the elastic moduli determined from this sample should clearly indicate the effect, if any, of hydrogarnet substitution.

EXPERIMENT

The hibschite sample used, GRR 1457, is a euhedral, transparent, colorless crystal ~200x300x300 mm in size from Crestmore, California [*Foshag*, 1920]. It was removed from an approximately 1-mm-thick vein of fine-grained calcium silicates in a hand specimen that was predominantly vesuvianite (Harvard Mineralogical Museum 81065). The chemical composition, as determined by electron microprobe analysis, is given in Table 1. Three random points were analyzed, and the crystal was found to be inhomogeneous in OH⁻ with x varying from 1.23-1.36. The values in Table 1 are

TABLE 1. Chemical Analysis of Hibschite 1457

Element	Atomic Ratio
Na	0.00
Mg	0.04
Al	1.87
Si	1.72
Ca	2.84
Mn	0.00
Fe	0.03
O*	12.00
H†	5.14

*Oxygen was analyzed directly.
†Calculated assuming (Si+H/4)=3.0.

an average of the three analyses. The lattice parameter, measured by single-crystal Xray diffraction using a Syntex P2₁ four-circle diffractometer, is given in Table 2, with the hydrous (grossular) and anhydrous (katoite) end-member values for comparison. Additionally, to interpret the Brillouin measurements it is necessary to know the index of refraction. Values for n_D and n_{514}, measured by immersion oil techniques, are also given in Table 2. The katoite end-member values were measured using a synthetic sample obtained from George Lager of the University of Louisville. Although lattice parameter values for the hydrogrossular series (see Figure 1a) show some scatter and the reported indices of refraction (Figure 1b) indicate a nonlinear trend (Figure 1b), our measurements are compatible with the average OH content of the sample, $x = 1.28$.

Seven of the natural growth faces of the hibschite were used for the Brillouin measurements. Optical goniometry was used to determine the orientation of each crystal face relative to the crystallographic axes in order to correct the velocity measurements for refraction effects [*Vaughan and Bass*, 1983]. Details of the Brillouin scattering technique are given by *Vaughan* [1979] and *Sandercock* [1982]. A 90° scattering geometry was used with a 514.5-nm wavelength light source supplied by an Ar-ion laser. Light scattered from the sample was analyzed by a plane-parallel piezoelectrically driven Fabry-Perot interferometer operated in a four-pass configuration. A full description of the system and the methods used is given by *Bass* [1989]. To avoid heating and dehydration of the sample during the experiment the laser power was reduced to less than 25 mW, and the run time was extended to 1-3 hours for each measurement. Table 3 gives the 29 acoustic velocities which were measured in 16 different crystallographic directions. All the measured velocities were corrected for surface refraction effects and then inverted to obtain the best fit set of elastic moduli, C_{ij} [*Weidner and Carleton*, 1977].

RESULTS

The hibschite elastic moduli determined from the velocity data set are given in Table 4. The uncertainties in Table 4 are 1 standard deviation calculated from the root-mean-square error in velocity of the entire data set for each modulus. Because of the inhomogeneity of the hydrous component in the sample, which affects the moduli through an uncertainty in density, the accuracy of the moduli is estimated to be at the 2 standard deviation level. The adiabatic bulk modulus K_S and the shear modulus μ, also given in Table 4, were calculated using both Voigt-Reuss-Hill averaging and Hashin-Shtrikman bounds [*Watt et al.*, 1976], with the results from the two methods being in complete agreement. The elastic constants for the anhydrous end-member grossular [*Bass*, 1989] are given for comparison in Table 4, as well as the isothermal bulk modulus K_0 of pure synthetic end-member katoite recently measured by static compression [*Olijnyk et al.*, 1991]. In comparing hibschite with grossular, a dramatic increase is seen in all the elastic moduli, such that shearing is affected similarly to bulk compression (see Figure 2). It should be pointed out that the elastic properties of silicate garnet have previously been observed to be remarkably constant with respect to changes in composition [*Bass*, 1986]. To emphasize the magnitude of the increased compressibility due to hydration, it can be compared, for reference, with the difference in moduli between the low- and high-pressure polymorphs of Mg_2SiO_4, olivine ($K_S = 129$ GPa, $\mu = 81$ GPa), and γ-spinel ($K_S = 184$ GPa, $\mu = 119$ GPa). The change of phase from olivine to γ-spinel effects a 30% difference in moduli, whereas in hibschite less than 50%

TABLE 2. Hydrogrossular $Ca_3Al_2(SiO_4)_{3-x}(H_4O_4)_x$ Properties

	Grossular*	Hibschite	Katoite
Lattice parameter, Å	11.851	12.183(3)	12.561(6)
Density, g/cm³	3.594	3.029	2.54
Refractive index			
n_D	1.734	1.661(3)	1.611(3)
$n_{514.5}$		1.670(3)	1.619(3)

The numbers in parenthesis are the uncertainty in the last digit.
*The properties of grossular ($x = 0$) are from *Skinner* [1956]; properties of hibschite ($0 < x < 1.5$) and katoite ($1.5 < x < 3.0$) are from this study (see text).

a)   Hydrogrossular Lattice Parameter

b)   Hydrogrossular Index of Refraction

Fig. 1. (a) Lattice parameters for the hydrogrossular series. Data are from *Flint et al.* [1941], *Cohen-Addad et al.* [1967], *Hazen and Finger* [1978], *Basso et al.* [1983], *Passaglia and Rinaldi* [1984], *Sacerdoti and Passaglia* [1985], *Lager et al.* [1987a], *Lager et al.* [1987b], *Bass* [1989], *Rinaldi and Passaglia* [1989], *Olijnyk et al.* [1991], *Knittle et al.* [1992], this study; with data of *Pabst* [1942], *Tilley* [1957], *Frankel* [1959], *Nalivkina* [1960], and *Bloxam* [1964] from tables of *Passaglia and Rinaldi* [1984]. (b) Index of refraction n_D for the hydrogrossular series. Data are from *Flint et al.* [1941], *Skinner* [1956], *Passaglia and Rinaldi* [1984] and this study; with data of *Belyankin and Petrov* [1941], *Pabst* [1942], *Hutton* [1943], *Frankel* [1959], *Nalivkina* [1960], and *Gross* [1977] from tables of *Passaglia and Rinaldi* [1984].

hydration of grossular causes a 40% change in the moduli. A 60% difference in moduli is seen between the completely hydrated katoite and grossular.

DISCUSSION

The high compressibility of hibschite can be understood in terms of the hydrogarnet crystal structure, which has been studied in detail by neutron and xray diffraction [*Sacerdoti and*

Passaglia, 1985; *Lager et al.*, 1987a, 1989; *Armbruster and Lager*, 1989]. The structure of garnet is shown in Figure 3, with the numbering scheme of *Novak and Gibbs* [1971] given in Figure 3a. Figures 3b and 3c show two consecutive layers of polyhedra in the unit cell separated by a/8 in the [001] direction. The unit cell is constructed of eight layers similar to these which are alternated and rotated, with each plane of cations separated by a/8. In hydrogarnet a substitution is made in the tetrahedron where $4H^+$ replace Si^{4+}, with the hydrogens being located outside and slightly above the face of the tetrahedron [*Lager et al.*, 1989; *Armbruster and Lager*, 1989]. With the $SiO_4 = H_4O_4$ substitution the O(1)-O(2) and O(1)-O(3) bonds lengthen substantially, from 2.56 Å and 2.74 Å, respectively, in grossular [*Hazen and Finger*, 1978] to 3.07 Å and 3.25 Å in fully hydrated (x = 3.00) katoite [*Lager et al.*, 1987a; *Cohen-Addad et al.*, 1967; *Bartl*, 1969]. A study of the vibrational spectra of hibschite under pressure by *Knittle et al.* [1992] indicates that this enlarged tetrahedron is responsible for the increased compressibility of hydrous garnets. The Raman spectra of hibschite and grossular show that with pressure H_4O_4 tetrahedra are reduced in size relatively more than SiO_4 tetrahedra. This may be due to an observed increase with pressure of hydrogen bonding between hydroxyl groups and neighboring oxygens, which would help to compress the H_4O_4 tetrahedron in hibschite. Additionally, the results of *Knittle et al.* [1992] show that the cation polyhedra in hibschite, including those tetrahedra containing silicon, have a similar response to pressure as is seen in grossular and therefore do not contribute to the increased compressibility of hydrous garnet.

We can examine what effect the high compressibility of this hydrated garnet phase would have on properties which are measurable in the mantle, such as density and sound velocity, and investigate the possible consequences of water structurally bound in mantle silicates. First, to consider density, we use the reaction

$$Ca_3Al_2(SiO_4)_3 + 2xH_2O = Ca_3Al_2(SiO_4)_{3-x}[(OH)4]_x + xSiO_2 \quad (1)$$
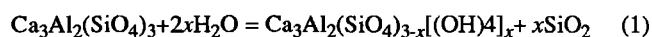
with x = 1.28 for the hibschite in this case. The Birch-Murnaghan equation of state was used to calculate the 300 K isothermal densities through the upper mantle for the assemblages on either side of the equation, grossular plus H_2O (ice VII) and hibschite plus stishovite (see Figure 4). *Olijnyk et al.* [1991] measured the pressure derivatives of the bulk moduli K_0' for grossular and the hydrous end-member katoite, as 6.1 and 4.1, respectively. These values were used to bracket the density of hibschite plus stishovite, with K_0' for hibschite assumed to be between the end-member values of 6.1 and 4.1. As seen in Figure 4, the assemblage with structurally bound H_2O (hibschite plus stishovite, shown bracketed by dashed lines) is denser than the assemblage with free H_2O as a separate phase to at least the top of the transition zone (~13 GPa).

In the temperature range of the upper mantle (~1600-1750 K from 3-13 GPa) the relative densities of the mineral phases would be affected by a trade-off between thermal expansion and increased compressibility. Perhaps the most dramatic difference would be shown by H_2O, which would be a liquid phase at mantle temperatures. The density of water at 1273 K has been calculated to 15 GPa [*Hill*, 1990], where it is ~2% less dense than our calculated density for ice VII at 300 K and the same pressure. Therefore we do not expect the outcome of our calculations to be significantly altered if extrapolated to high

TABLE 3. Velocities Measured From Hibschite 1457

Wave Normal*			Velocities Observed[†], km/s			Velocities Calculated, km/s		
N_a	N_b	N_c	V_p	V_{s1}	V_{s2}	V_p	V_{s1}	V_{s2}
0.678	–0.554	0.484	7.86			7.82		
0.679	–0.502	0.536		4.60			4.61	
0.809	–0.400	0.431	7.91	4.71		7.82	4.61	
0.920	–0.257	0.296	7.79	4.64		7.84	4.60	
–0.623	–0.503	0.600	7.81	4.66		7.82	4.62	
–0.214	–0.651	0.728	7.84	4.68		7.82	4.63	
–0.054	–0.044	0.998	7.84	4.46		7.85	4.59	
0.475	0.062	0.878		4.48			4.59	
0.048	0.017	0.999	7.79	4.60		7.85	4.59	
0.470	0.059	0.881	7.81	4.58		7.83	4.59	
0.439	0.043	0.898	7.85	4.60	4.68	7.83	4.59	4.62
0.481	0.085	0.873	7.68	4.57		7.83	4.59	
0.057	–0.053	0.997	7.79	4.58		7.85	4.59	
0.720	–0.526	0.453	7.87			7.82		
0.747	–0.421	0.514	7.84			7.82		
0.138	–0.693	0.707	7.88			7.82		
0.100	–0.673	0.733	7.91			7.82		
–0.004	–0.273	0.962	7.81			7.84		

The rms deviation is 0.06 km/s.
*The acoustic wave normal is given in terms of direction cosines with respect to the three crystallographic axes.
[†]Shear wave polarizations are known.

temperature, provided the stability field of hydrogrossular is not exceeded.

Although hibschite and katoite have been shown to be stable at pressures encompassing those of the entire upper mantle, at room temperature [*Knittle et al.*, 1992; *Olijnyk et al.*, 1991], similar to phase B, the extent of the stability of hydrous garnet under complete mantle conditions is an open question. It may be argued, however, from the estimates of natural hydrous garnet equilibration at depths as great as 180 km, along with the results shown in Figure 4, that hydrogrossular could act as a vehicle for water transport to great depths and for water storage in the mantle, particularly in areas of subducting oceanic crust.

When the hydrogarnet substitution is made ($H_4O_4 = SiO_4$), it has been observed that one of the ways the expanded tetrahedron is accommodated is by a decrease in the shared octahedral edge length, O(1)-O(4) (see Figure 3a) and an increase in the length of the unshared edge, O(1)-O(5) [*Lager et al.*, 1987a]. This octahedral distortion increases with the amount of hydrous component. In grossular the shared octahedral edge is longer than the unshared edge [*Hazen and Finger*, 1978], and the octahedral distortion is easily accommodated. However, in pyrope $Mg_3Al_2Si_3O_{12}$ the octahedral shared edge is shorter than the unshared edge, so that a hydrous component may not be easily incorporated [*Sacerdoti and Passaglia*, 1985; *Lager et al.*, 1987a]. This is supported with evidence from natural and synthetic pyropes which typically have < 1 wt % H_2O [*Geiger et al.*, 1991; *Lager*

et al., 1987a; *Lager et al.*, 1989; *Aines and Rossman*, 1984; *Ackermann et al.*, 1983]. Therefore eclogitic regions of the mantle, which contain a higher proportion of Ca-bearing garnet, such as the pressure-transformed basaltic portion of subducted slabs, are likely locations for a significant component of hydrogrossular.

A logical question to examine is how the properties of eclogite with water-bearing garnet compare with those of a dry composition. Because seismic waves are the most direct method of probing the mantle, we have calculated the seismic wave velocities for a model eclogite. Starting with an assemblage of 50% omphacite and 50% grossular by volume, the longitudinal and shear seismic velocities V_p and V_s were calculated along a 300 K adiabat, using the bulk and shear moduli measured by *Bhagat and Bass* [1992] for omphacite and by *Bass* [1989] for grossular. Pressure derivatives of the moduli for both phases are from *Duffy and Anderson* [1989]. The calculated seismic velocities for dry eclogite are compared in Figures 5a and 5b with those calculated for wet eclogite, where hibschite substitutes completely for the grossular component. The seismic velocities in the wet eclogite are ~6-8% slower than in dry eclogite. The value of K_0' used for hibschite was determined by linear interpolation between the values of K_0' for grossular, 6.1, and katoite, 4.1. We note, however, the values of K_0 measured across the hydrogrossular series demonstrate a nonlinear relation (Figure 2). Mineral garnets, which have substitution on the Ca or Al site, do not

TABLE 4. Elastic Properties

	C_{11}*	C_{12}	C_{44}	K	μ
Hibschite	186.5(11)	56.5(14)	63.9(5)	99.8(10)	64.3(5)
Grossular[†]	321.7(8)	91.4(9)	104.6(4)	168.4(7)	108.9(4)
Katoite[‡]				66(4)	

The numbers in parenthesis are the uncertainty in the last digit.
* All elastic moduli are given in units of gigapascals.
[†] From *Bass* [1989].
[‡] From *Olijnyk et al.* [1991].

Hydrogrossular Bulk and Shear Moduli
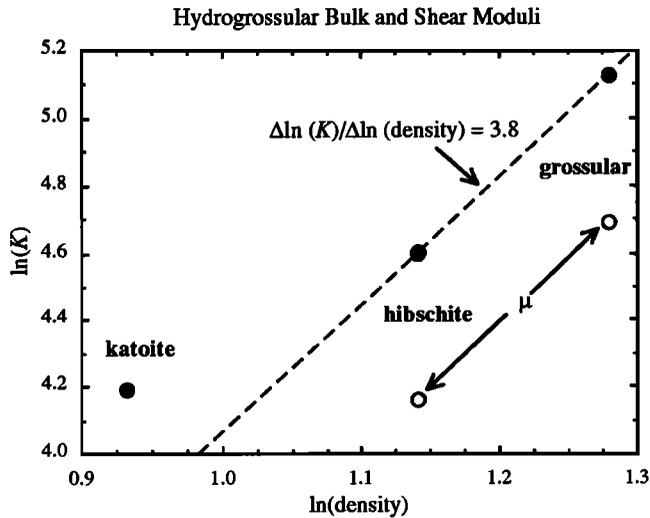
Fig. 2. Measured bulk and shear moduli K and μ for hydrogrossular series $Ca_3Al_2(SiO_4)_{3-x}(H_4O_4)_x$ (see Table 4). Data are from *Olijnyk et al.* [1991] for katoite ($x = 3.0$), from *Bass* [1989] for grossular ($x=0.0$), and from this study for hibschite ($x = 1.28$). A nonlinear relation is seen between K and H_2O content ($x = 3.0$ is completely hydrated); however, between grossular and hibschite, $\Delta\ln(K)/\Delta\ln(\rho) = 3.8$, indicating the difference in compressibility may largely be a volume effect (see discussion). Also, note the decrease of K due to H_2O substitution is similar to the decrease of μ.

provide systematics to determine whether K_0' behaves nonlinearly also, and the value can only be bracketed by the end-members. However, if the value of K_0' for hibschite is closer to that of katoite, a greater difference in velocities between the wet and dry eclogite models would result.

The limit for seismological resolution is, conservatively, a travel time delay of 0.5 s in V_p. Such a travel time delay can be the result of a seismic wave traveling for a short distance through an area with a large velocity decrease or, conversely, following a long path through an area with a small velocity decrease. Given the velocity difference between the wet and dry eclogite models, a P wave traveling through 45 km of wet eclogite would be 0.5 s slower than the same wave passing through dry eclogite. In other words, for any thickness of eclogite less than 45 km the P wave travel time delay would be below the limit of resolution, and it would not be possible to differentiate between wet or dry eclogite. On the basis of oceanic crustal thickness, a subduction zone eclogite layer might be on the order of 10 km thick rather than 45 km thick (although it may be in the form of a sheet with broader dimensions), and the amount of grossular (or hibschite) in the eclogite might range up to only slightly more than 50% of the entire garnet component [*Dawson*, 1980] rather than the 100% of the model. If water is carried into the mantle by subducted crustal layers [*Peacock*, 1990; *von Huene and Scholl*, 1991; *Meade and Jeanloz*, 1991; *Moore and Vrolijk*, 1992], these factors combine to reduce the observability of areas that may be saturated with hydrous minerals. Therefore it is possible for a considerable amount of water to be stored, undetected, within the mantle. For example, a mass of H_2O equivalent to that of the hydrosphere ($\sim$1.4 x 10^{21} kg H_2O) would be contained within $\sim$8.5 x 10^9 km^3 of our wet model eclogite (1.35 wt % H_2O, 4.78 mol % H_2O). If this amount of eclogite, $\sim$3 vol % of the upper mantle, were distributed throughout the mantle in such a way that the dimensions were less than 45 km in any given direction (that is, below the limit of seismic resolution)

an invisible ocean of water could be stored in the upper mantle. Generally, tomographic studies of the upper mantle which
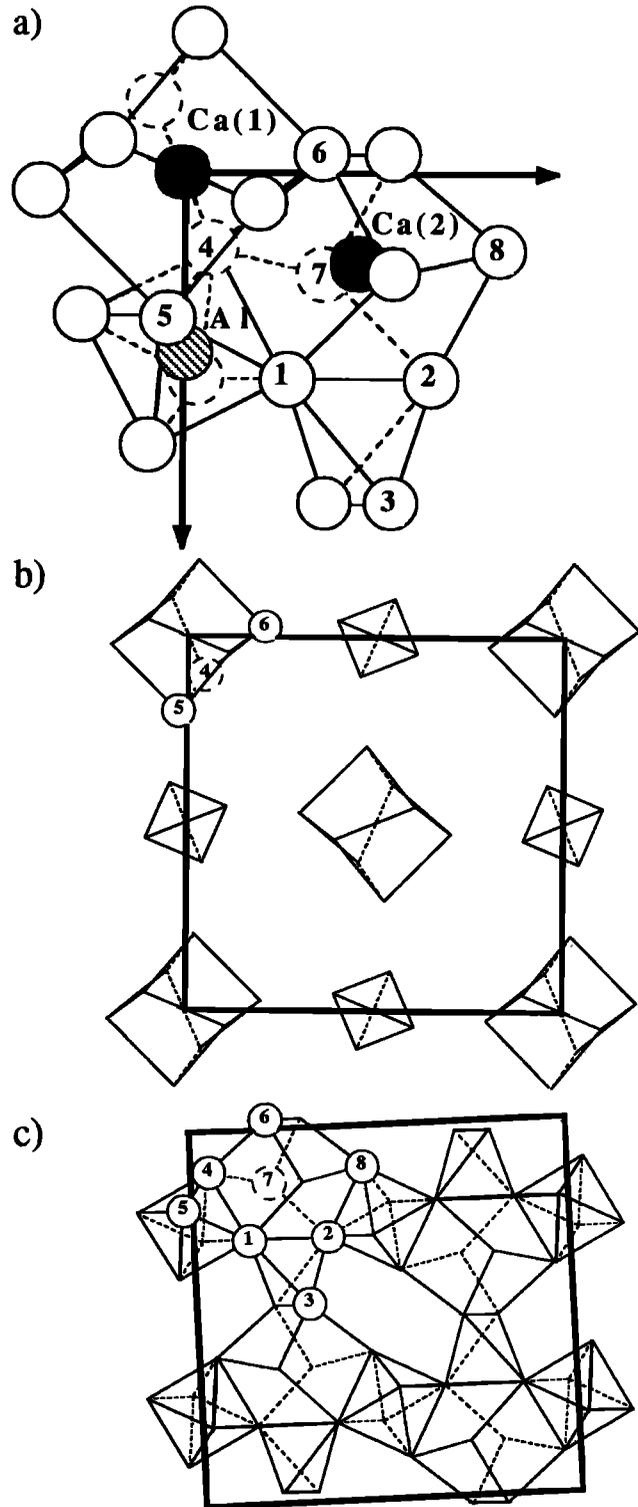
Fig. 3. (a) Four polyhedra in the garnet structure, showing the numbering scheme of *Novak and Gibbs* [1971]. The solid lines indicate the unit cell edges. (b)-(c) Two layers of the garnet structure projected in the 001 direction. The plane of cations in (b) are located a distance a/8 above those in (c). The locations of Ca and Al are shown in (a). In grossular, Si occupies the middle of each tetrahedron. In hydrogrossular an Si atom is replaced with four H atoms located outside the tetrahedron, one slightly above each face.
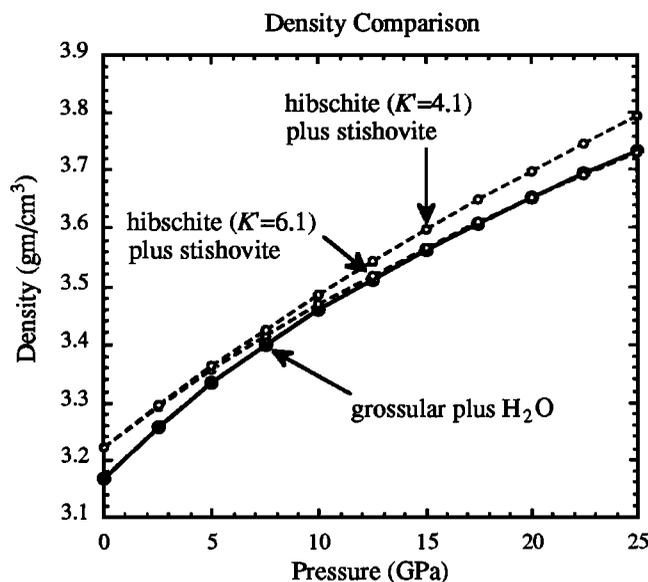
Fig. 4. The 300 K isothermal densities for two chemically equivalent compositions. Solid circles indicate grossular plus H_2O, and open circles indicate hibschite plus stishovite. The assemblage with bound water is denser through the upper mantle (pressure $\leq$ 22 GPa). Isothermal bulk moduli K_{T0} of grossular and hibschite are estimated from K_{S0} measured by *Bass* [1989] (grossular) and this study (hibschite) assuming a thermal expansion coefficient, α=20x10^{-6} K^{-1}, and Grüneisen parameter γ=1.5. K_0' for hibschite is assumed to be between the katoite-grossular series end-member values [*Bass*, 1989; *Olijnyk et al.*, 1991] which are used to bracket the high-pressure density of hibschite plus stishovite. K_{S0} and K_0' for stishovite are from *Duffy and Anderson* [1989] with K_{T0} estimated using assumed values of α and γ of 15x10^{-6} K^{-1} and 1.5, respectively. The properties of ice VII, the stable phase of H_2O at the conditions of the calculation, are from *Hemley et al.* [1987].

make any inferences about lateral variations in seismic velocities correlate these variations to temperature differences. Figure 5 illustrates the effect of temperature on the seismic velocities of the model eclogite in comparison with various degrees of hydration. For example, based upon the seismic velocities it would not be possible to distinguish between a 10% hydration of the garnet component and a 400° increase in the eclogite temperature (from 300 K to 700 K). The results shown in Figure 5 demonstrate that decoupling the effect of temperature and H_2O content on seismic velocity may prove difficult, and indicate that hydrous minerals may be responsible for some of the seismically observed heterogeneity in the upper mantle.

Conclusions

Hibschite, a hydrogarnet with approximately 42% H_4O_4 substitution for SiO_4, is found to have ~40% greater bulk and shear compressibilities than grossular, the anhydrous counterpart. The crystal chemical basis for the increased compressibility of hydrogrossular is probably the larger volume of the H_4O_4 tetrahedron as compared with the smaller, more rigid SiO_4 tetrahedron in silicate garnets. A result of this increased compliance is that through the pressure range of the upper mantle structurally bound H_2O in garnet has a greater density than garnet coexisting with a separate solid H_2O phase. Therefore hydrogarnet is likely to be thermodynamically preferred at high pressure. Although the seismic velocities of hibschite are ~16% slower than those of grossular, when considered in the context of an eclogitic rock

composition, a large volume of hydrated garnet is required before a substantial delay in seismic wave travel times would be observed. Additionally, unless there are differences in seismic wave attenuation, a slowness in velocity due to a warmer region of the mantle may be alternatively interpreted as hydration [*Bonatti*, 1990]. Since it is anticipated that other hydrous phases will show a similar slowness in seismic velocity compared to their anhydrous equivalents [*Tyburczy et al.*, 1991], it is plausible that a considerable amount of water may be stored, unseen or unrecognized, in the Earth's mantle.
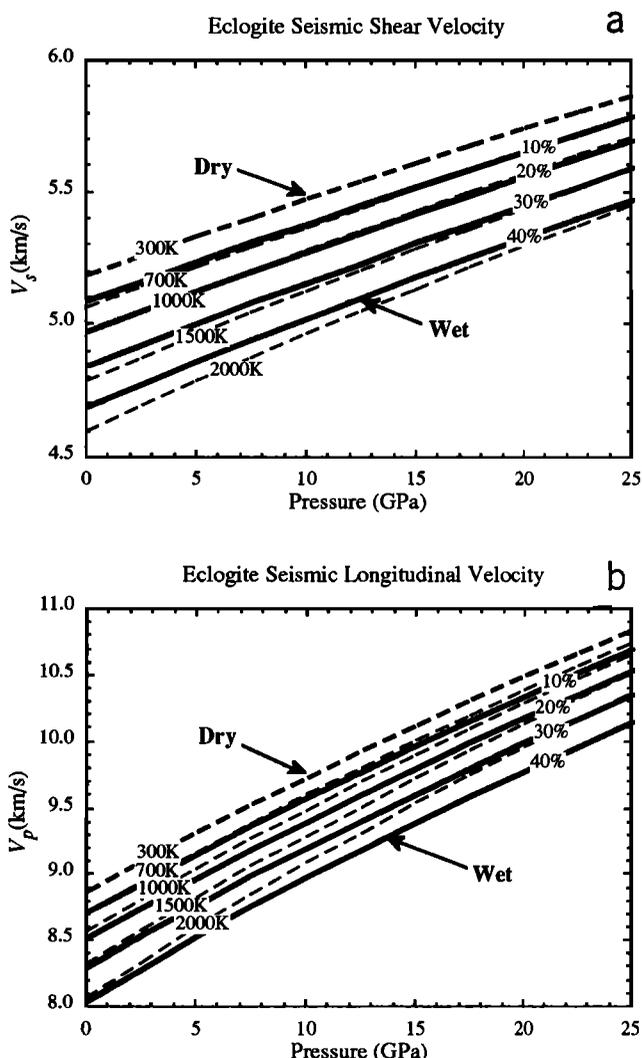
Fig. 5. Seismic velocities for a model eclogite consisting of 50% omphacite and 50% grossular calculated along a 300 K adiabat (dashed line labeled "dry"). Solid lines, also calculated along 300 K adiabats, are for eclogite, with the grossular component replaced by hydrogrossular $Ca_3Al_2(SiO_4)_{3-x}(H_4O_4)_x$, where x = 0.32, 0.64, 0.96, and 1.28 for 10%, 20%, 30%, and 40% hydration, respectively. The curve labeled "wet" represents a model eclogite consisting of 50% omphacite and 50% hibschite GRR 1457, specifically. Other dashed lines are for seismic velocities for "dry" eclogite calculated along 700 K, 1000 K, 1500 K, and 2000 K adiabats.

REFERENCES

Ackermann, L., L. Cemic, and K. Langer, Hydrogarnet substitution in pyrope: A possible location for "water" in the mantle, Earth Planet. Sci. Lett., 62, 208–214, 1983.

Ahrens, T. J., Water storage in the mantle, Nature, 342, 122–123, 1989.

Aines, R. D., and G. R. Rossman, Water content of mantle garnets, Geology, 12, 720–723, 1984.

Akaogi, M., and S. J. Akimoto, High-pressure stability of a dense hydrous magnesian silicate $Mg_{23}Si_8O_{42}H_6$ and some geophysical implications, J. Geophys. Res., 85, 6944–6948, 1980.

Armbruster, T., and G. A. Lager, Oxygen disorder and the hydrogen position in garnet-hydrogarnet solid solutions, Eur. J. Mineral., 1, 363–369, 1989.

Bartl, H., Röntgen-Einkristalluntersuchungen an $3CaO \cdot Al_2O_3 \cdot 6H_2O$ und an $12CaO \cdot 7Al_2O_3 \cdot H_2O$: Neuer Vorschalg zur $CaO \cdot 7Al_2O_3$ Struktur, Neues Jahrb. Mineral. Monatsh., 404–413, 1969.

Bass, J. D., Elasticity of uvarovite and andradite garnets, J. Geophys. Res., 91, 7575–7516, 1986.

Bass, J. D., Elasticity of grossular and spessartite garnets by Brillouin spectroscopy, J. Geophys. Res., 94, 7621–7628, 1989.

Basso, R., A. Della Giusta, and L. Zefiro, Crystal structure refinement of plazolite: A highly hydrated natural hydrogrossular, Neues Jahrb. Mineral. Monatsh., 6, 251–258, 1983.

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

Bell, R. D., and G. R. Rossman, The distribution of hydroxyl in garnets from the subcontinental mantle of southern Africa, Contrib. Mineral. Petrol., 111, 161–178, 1992b.

Belyankin, D. S., and V. P. Petrov, The grossularoid group (hibschite, plazolite), Amer. Mineral., 26, 450–453, 1941.

Bhagat, S., and J. D. Bass, Single-crystal elastic properties of omphacite-C2/c by Brillouin spectroscopy, J. Geophys. Res., 97, 6843–6848, 1992.

Bloxam, T. W., Hydrogrossular from the Grivan-Ballantrae complex, Ayrshire, Mineral. Mag., 33, 814–815, 1964.

Bonatti, E., Not so hot "hot spots" in the oceanic mantle, Science, 250, 107–111, 1990.

Cohen-Addad, C., P. Ducros, and E. F. Bertaut, Etude de las substitution du groupement SiO_4 par $(OH)_4$ dans les composés $Al_2Ca_3(OH)_{12}$ et $Al_2Ca_3(SiO_4)_{2.16}(OH)_{3.36}$ de type grenat, Acta Crystallogr., 23, 220–230, 1967.

Dawson, J. B., Kimberlites and Their Xenoliths, pp. 168–172, Springer-Verlag, New York, 1980.

Duffy, T. S., and D. L. Anderson, Seismic velocities in mantle minerals and the mineralogy of the upper mantle, J. Geophys. Res., 94, 1895–1912, 1989.

Finger, L. W., J. Ko, R. M. Hazen, T. Gasparik, R. J. Hemley, C. T. Prewitt, and D. J. Weidner, Crystal chemistry of phase B and an anhydrous analogue: Implications for water storage in the upper mantle, Nature, 341, 140–142, 1989.

Flint, E. P., H. F. McMurdie, and L. S. Wells, Hydrothermal and x-ray studies of the garnet-hydrogarnet series and the relationship of the series to hydration products of portland cement, J. Res. Natl. Bur. Stand., 26, 13–33, 1941.

Foshag, W. F., Plazolite, a new mineral, Amer. Miner., 5, 183–185, 1920.

Frankel, J. J., Uvarovite garnet and South African jade (hydrogrossular) from the Bushveld complex, Transvaal, Amer. Mineral., 44, 565–591, 1959.

Geiger, C. A., K. Langer, D. R. Bell, G. R. Rossman, and B. Winkler, The hydroxide component in synthetic pyrope, Am. Mineral., 76, 49–59, 1991.

Gross, S., The mineralogy of the Hatrurim formation, Israel, Geol. Surv. Israel, Bull. No. 70, 1–80, 1977.

Hazen, R. M., and L. W. Finger, Crystal structures and compressibilities of pyrope and grossular to 60 kbar, Am. Mineral., 63, 297–303, 1978.

Hemley, R. J., A. P. Jephcoat, H. K. Mao, C. S. Zha, L. W. Finger, and D. E. Cox, Static compression of H_2O-ice to 128 GPa (1.28 Mbar), Nature, 330, 737–740, 1987.

Hill, P. G., A unified fundamental equation for the thermodynamic properties of H_2O, J. Phys. Chem. Ref. Data, 19, 1233–1274, 1990.

Hutton, C. O., Hydrogrossular, a new mineral of the garnet-hydrogarnet series, Trans. Roy. Soc. New Zealand, 73, 174–180, 1943.

Knittle, E., A. Hathorne, M. Davis, and Q. Williams, A spectroscopic study of the high-pressure behavior of the O_4H_4 substitution in garnet, in High-Pressure Research: Application to Earth and Planetary Sciences, Geophys. Monogr. Ser., vol. 67, edited by Y. Syono and M.

H. Manghnani, pp. 297–304, AGU, Washington, D.C., 1992.

Lager, G. A., T. Armbruster, and J. Faber, Neutron and x-ray diffraction study of hydrogarnet $Ca_3Al_2(O_4H_4)_3$, Am. Mineral., 72, 756–765, 1987a.

Lager, G. A., G. R. Rossman, F. J. Rotella, and A. J. Schultz, Neutron-diffraction structure of a low-water grossular at 20 K, Amer. Miner., 72, 766–768, 1987b.

Lager, G. A., T. Armbruster, F. J. Rotella, and G. R. Rossman, OH substitution in garnets: X-ray and neutron diffraction, infrared, and geometric-modeling studies, Am. Mineral., 74, 840–851, 1989.

Martin, R. F., and G. Donnay, Hydroxyl in the mantle, Am. Mineral., 57, 554–570, 1972.

Meade, C., and R. Jeanloz, Deep-focus earthquakes and recycling of water into the earth's mantle, Science, 252, 68–72, 1991.

Moore, J. C., and P. Vrolijk, Fluids in accretionary prisms, Rev. Geophys., 30, 113–135, 1992.

Nalivkina, E. B., Hibschite from near the Bug River, Zapiski Vses. Mineralog. Obshch. (Mem. All-Union Min. Soc.), 89, 717–718 (in Russian) (Mineral Abs., 16, 454), 1960.

Novak, G. A., and G. V. Gibbs, The crystal chemistry of silicate garnets, Am. Mineral., 56, 791–825, 1971.

Olijnyk, H., E. Paris, C. A. Geiger, and G. A. Lager, Compressional study of katoite $[Ca_3Al_2(O_4H_4)_3]$ and grossular garnet, J. Geophys. Res., 96, 14,313–14,318, 1991.

Pabst, A., The crystal structure of plazolite, Amer. Mineral., 22, 861–868, 1937.

Passaglia, E., and R. Rinaldi, Katoite, a new member of the $Ca_3Al_2(SiO_4)_3$-$Ca_3Al_2(OH)_{12}$ series and a new nomenclature for the hydrogrossular group of minerals, Bull. Mineral., 107, 605–618, 1984.

Peacock, S. M., Fluid processes in subduction zones, Science, 248, 329–337, 1990.

Rinaldi, R., and E. Passaglia, Hibschite topotype: Crystal chemical characterization, Eur. J. Mineral., 1, 639–644, 1989.

Ringwood, A. E., and A. Major, High-pressure reconnaissance investigations in the system Mg_2SiO_4-MgO-H_2O, Earth Planet. Sci. Lett., 2, 130–133, 1967.

Rossman, G. R., and R. D. Aines, The hydrous components of garnets: Grossular-hydrogrossular, Am. Mineral., 76, 1153–1164, 1991.

Sacerdoti, M. and E. Passaglia, The crystal structure of katoite and implications within the hydrogrossular group of minerals, Bull. Mineral., 108, 1–8, 1985.

Sandercock, J. R., Trends in Brillouin scattering: Studies of opaque materials, supported films, and central modes, in Light Scattering in Solids III, Top. Appl. Phys., vol. 15, edited by M. Cardona and G. Gunterhodt, pp. 173–206, Springer-Verlag, New York, 1982.

Skinner, B. J., Physical properties of end-members of the garnet group, Am. Mineral., 41, 428–436, 1956.

Thompson, A. B., Water in the Earth's upper mantle, Nature, 358, 295–302, 1992.

Tilley, C. E., On the replacement of anorthosite by hydrogrossular in the Transvaal, Trans. Geol. Soc. South Africa, 60, 15, 1957.

Tyburczy, J. A., T. S. Duffy, T. J. Ahrens and M. A. Lange, Shock wave equation of state of serpentine to 150 GPa: Implications for the occurrence of water in the earth's lower mantle, J. Geophys. Res., 96, 18,011–18,027, 1991.

Vaughan, M. T., Elasticity and crystal structure in aluminosilicates and pyroxenes, Ph. D. thesis, State Univ. of N. Y., at Stony Brook, 1979.

Vaughan, M. T., and J. D. Bass, Single crystal elastic properties of protoenstatite, Phys. Chem. Miner, 10, 62–68, 1983.

von Huene, R., and D. W. Scholl, Observations at convergent margins concerning sediment subduction, subduction erosion, and the growth of continental crust, Rev. Geophys., 29, 279–316, 1991.

Watt, J. P., G. F. Davies, and R. J. O'Connell, The elastic properties of composite materials, Rev. Geophys., 14, 541–563, 1976.

Weidner, D. J., and H. R. Carleton, Elasticity of coesite, J. Geophys. Res., 82, 1334–1346, 1977.

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