

HYDROGARNET: MULTI-SITE HYDROGEN OCCUPANCY IN THE GARNET STRUCTURE

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ABSTRACT

Hydrogarnet from low-grade metamorphic rocks in the Quebec Appalachians has a relatively large unit-cell (approximately 12.2 Å) and low index of refraction (approximately 1.786). Fe-Mn zoning is common in these grains. Calculated formulae do not agree with the hydrogarnet formula, in which H_4O_4 substitutes for SiO_4 tetrahedra, but require the presence of hydroxyl groups in another position in the structure.

Keywords: hydrogarnet, OH-for-O substitution, Quebec Appalachians, low-grade metamorphism.

SOMMAIRE

L'hydrogrenat des roches faiblement métamorphisées des Appalaches québécoises a un paramètre réticulaire d'environ 12.2 Å et un indice de réfraction d'environ 1.786, valeurs relativement élevée et basse, respectivement, en comparaison des valeurs attendues du grenat dans de telles roches métamorphiques. Une zonation en Fe et Mn est courante dans ces cristaux. Les formules calculées ne correspondent pas à la formule acceptée de l'hydrogrenat, où le groupe H_4O_4 remplace un tétraèdre SiO_4 . Les groupes hydroxyles occuperaient une autre position dans la structure.

Mots-clés: hydrogrenat, substitution de OH pour O, Appalaches québécoises, faible métamorphisme.

INTRODUCTION

Compositional variety and sensitive response to changing pressure and temperature place garnet among the most useful minerals in studies of geothermometry. The first appearance of abundant Fe-rich, Mn-poor garnet marks an isograd in metamorphosed mafic and clastic sedimentary rocks (Miyashiro 1973, Turner 1968). To date, well-characterized examples of low-temperature manganiferous garnet have been relatively little studied. Harte & Graham (1975) observed that Mn was probably distributed among gar-

net and coexisting minerals at a close approach to equilibrium. Wilkins & Sabine (1973) reported 2.57 and 2.50% H_2O in spessartine. Hsu (1980) studied the hydration and phase relations of spessartine at 2 kbar water pressure; he established that end-member hydrospeessartine has no stability field under the conditions of his experiments.

By analogy with materials isotypic with garnet (McConnell 1942, Pabst 1937, 1942, Flint *et al.* 1941), Hutton (1943) deduced that hydrogen enters the garnet structure by the substitution of H_4O_4 for SiO_4 . Here we report the results of electron-probe, infrared-absorption spectroscopy and X-ray-diffraction studies of naturally occurring hydrogarnet. The garnet occurs as 30- to 100- μ m crystals in schists; it is zoned in Mn, Fe, Ca, Si and H. We deduce a multi-site occupancy for hydrogen in these grains. If our deduction is accepted, some revision of the naming of garnets will be required, as there will be at least two mechanisms of hydrogen substitution in this family of minerals. Further studies of hydrogarnet may lead to an increased understanding of the nature and evolution of fluids in rocks during metamorphism.

REGIONAL GEOLOGY

Four samples of garnet-bearing rock were collected in a study of the metamorphic evolution of the Thetford Mines area in the Quebec Appalachians (Birkett 1982). The four samples are metasedimentary rocks from the Bennett Schist, a low-grade metamorphic terrane of probable lower Paleozoic age that forms the core of the Notre-Dame anticlinorium (St-Julien & Hubert 1975). In the area of the garnetiferous samples, the rocks have been metamorphosed to the chlorite zone of the greenschist facies. Mafic rocks, never far from the outcrops of garnet-bearing metasediments, contain chlorite, actinolite, albite, epidote, calcite, quartz, white mica and Fe-Ti oxide.

THE SAMPLES

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Sample descriptions, locations, infrared-absorption spectra, X-ray powder patterns and

TABLE 1. REPRESENTATIVE COMPOSITION OF HYDROGARNET SAMPLES

	SC2-9	16216	168-3	16810	39814	399-6	39916	39917	HG1-C	HG2-A
SiO ₂	37.53	37.55	38.53	37.00	38.14	36.60	37.50	36.81	26.86	35.51
TiO ₂	0.23	0.16	0.17	0.08	0.32	0.20	n.d.	0.63	n.d.	n.d.
Al ₂ O ₃	20.64	20.53	21.52	20.65	19.41	19.70	20.19	19.43	22.34	21.24
FeO ¹	8.31	13.14	10.93	17.49	9.53	7.18	20.77	6.90	0.70 ³	0.66 ³
MnO	20.72	17.29	12.63	7.93	20.76	23.33	10.96	22.10	n.d.	0.25
MgO	0.46	0.32	0.52	1.82	n.d.	n.d.	0.84	n.d.	n.d.	n.d.
CaO	5.97	13.46	14.04	11.77	5.10	3.42	3.36	3.71	39.46	38.70
Na ₂ O	n.d.	n.d.	n.d.	n.d.	n.d.	0.24	0.29	n.d.	n.d.	n.d.
K ₂ O	0.36	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
H ₂ O ²	5.79	3.55	1.64	3.26	6.74	9.22	6.05	10.42	10.64	3.64
Si	2.762	2.835	2.953	2.807	2.781	2.603	2.766	2.566	1.8762	2.6119
Ti	0.013	0.009	0.10	0.005	0.018	0.011	0.000	0.033	0.000	0.000
Al	1.791	1.827	1.945	1.847	1.668	1.651	1.756	1.597	1.8397	1.8418
Fe ³⁺	0.512	0.830	0.701	1.110	0.581	0.427	1.281	0.402	0.0386 ⁴	0.0365 ⁴
Mn ²⁺	1.292	0.722	0.820	0.510	1.282	1.405	0.685	1.305	0.000	0.0156
Mg	0.051	0.036	0.059	0.206	0.000	0.000	0.092	0.000	0.000	0.000
Ca	0.471	1.089	1.153	0.957	0.398	0.261	0.266	0.277	2.9535	3.0501
Na	0.000	0.000	0.000	0.000	0.000	0.033	0.042	0.000	0.000	0.000
K	0.034	0.000	0.000	0.000	0.000	0.010	0.004	0.000	0.000	0.000
H	2.844	1.788	0.849	1.650	3.278	4.364	2.977	4.846	4.9585	1.7862

¹. Total iron as FeO; ². H₂O by difference; ³. Total iron as Fe₂O₃; ⁴. Fe³⁺;
n.d. not detected. Formulae calculated on the basis of twelve atoms of oxygen.

electron-probe data on the garnet samples and co-existing minerals are on deposit with The Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

Initial electron-probe determinations of the compositions of garnet reported here gave totals of the oxides detected systematically below 100% by weight. Since other minerals analyzed concurrently with garnet gave acceptable totals, we widened the data base for this study by including two samples of garnet-bearing iron-formation from the Sherbrooke area provided by S. Chevé (pers. comm.). These samples are referred to as SC1 and SC2. Electron-microprobe analyses of garnet in these samples by Chevé had also given low totals (pers. comm., 1978). With the assistance of H. R. Steacy of the Geological Survey of Canada, we obtained two samples of hydrogrossular: HG1, Mt. Mineoka, Chibu

Prefecture, Japan, and HG2, "pink jade" from Buffelsfontein, Rustenberg, Transvaal, South Africa. Sample HG2 comes from material donated to the Mineralogical Museum of the Geological Survey of Canada by P.G. Manning, and is similar to material described in Manning & Owens (1977), although optical and electron-probe examination of our sample show only a single garnet phase.

BULK COMPOSITION OF THE HYDROGARNET

Electron-microprobe analyses (by energy dispersion) were obtained for garnet in polished thin sections. Accelerating voltage was 15 kV, and sample current was 20 nA measured on benitoite. Spectra were acquired for a counting time of 100 seconds. Standards used in this study are well-analyzed, homogeneous, natural and synthetic silicates and oxides. Data acquisition and reduction were done on an automated KEVEX 7000 EDS system.

Representative compositions of hydrogarnet and hydrogrossular are presented in Table 1. In the case of hydrogarnet, oxide totals exclusive of H₂O are systematically less than 100%. Other minerals analyzed concurrently in the course of this study give totals and calculated stoichiometries that are satisfactory. The total for garnet, therefore, cannot be rejected without further investigation.

The grains of garnet are zoned with respect to Fe and Mn, although in a patchy rather than a concentric pattern. No birefringence was noted.

X-RAY-DIFFRACTION STUDIES

X-ray-diffraction data for hydrogarnet from three samples are listed in Table 2. Garnet fragments removed from uncovered thin sections were attached

TABLE 2. X-RAY-DIFFRACTION DATA FOR HYDROGARNET

hkl	76162		76168		77399	
	I	d	I	d	I	d
211	<5	4.98			<5	4.62
220			5	4.35		
310	<5	3.68			<5	3.87
321	5	3.29	<5	3.43	5	3.48
400	40	3.06	50	3.08	50	3.06
420	100	2.73	100	2.75	100	2.71
422	15	2.49	5	2.51	10	2.48
510,431	10	2.38	5	2.39	5	2.38
521	15	2.24	10	2.24	5	2.22
530,433	<5	2.08				
611,532	20	1.98	20	1.99	10	1.96
444	10	1.76	10	1.76	15	1.75
640	15	1.68	20	1.69	20	1.68
642	30	1.62	20	1.63	30	1.62
800	5	1.51	5	1.52	10	1.50
910,833	5	1.35			5	1.34
a (Å)	12.204		12.192		12.125	
s.e. (Å)	0.006		0.003		0.004	
n					1.786 ± 0.001	

a is calculated by least-squares refinement of selected diffraction maxima. s.e.: standard error associated with the refinement.

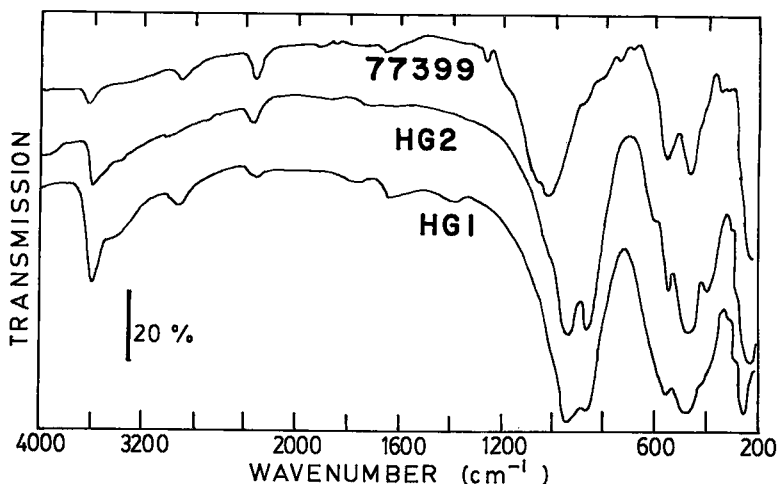


FIG. 1. Infrared-absorption spectra from 200 to 4000 cm^{-1} , for samples 77399, HG1 and HG2.

to glass fibres with vaseline to provide mounts suitable for a 57.3-mm-diameter Debye-Scherrer powder camera (Ni-filtered $\text{CuK}\alpha$ radiation).

The three films obtained from the samples of hydrogarnet record lines that are vague and broad, attributed to the zoning of Fe and Mn, detected elsewhere with the electron probe. Despite the large standard deviation associated with the estimates of the unit-cell dimension of the garnet (Table 2), the cell size is significantly larger than that of anhydrous garnet of approximately the same composition ($a = 12.2$ versus 11.7 \AA , Deer *et al.* 1962). Comparisons with the change in cell dimension between other hydrogarnet compositions and their anhydrous equivalents are not justified, in that the location of the hydrogen ion in the structure determines how effectively it will expand the cell size.

INFRARED-ABSORPTION STUDIES

Infrared-absorption spectra of garnet separates from 77399, HG1 and HG2 were obtained with a Beckman IR12 spectrophotometer. Approximately 2 mg of sample were mixed with 200 mg of KBr, ground under acetone, dried, and pressed into a clear disk. All materials were dried 48 hours in a desiccating oven prior to final preparation of samples. All measurements are made in comparison to a blank disk, prepared with the sample disks. Small absorption bands between 3200 and 1300 cm^{-1} are due to differences in the acetone content of the sample and blank disks.

All three spectra (Figs. 1, 2) show O-H absorption bands at 3620 cm^{-1} . The intensity of the absorption correlates with the H_2O content of the minerals, as calculated by difference (Table 1). The

Si-O absorption bands in HG1 (935, 870, 550, 470 cm^{-1}) cannot be distinguished in wavenumber from HG2 (930, 860, 555, 470 cm^{-1}) despite the large

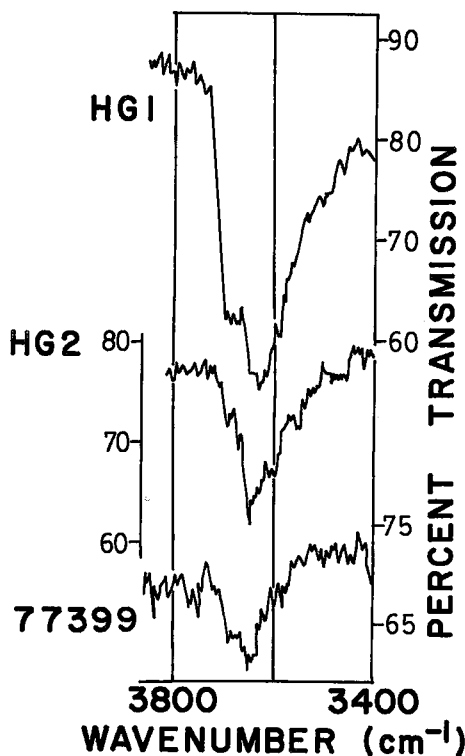


FIG. 2. Detail of half-speed scans in the infrared-absorption spectra of 77399, HG1 and HG2 in the region of the O-H stretching band at 3620 cm^{-1} .

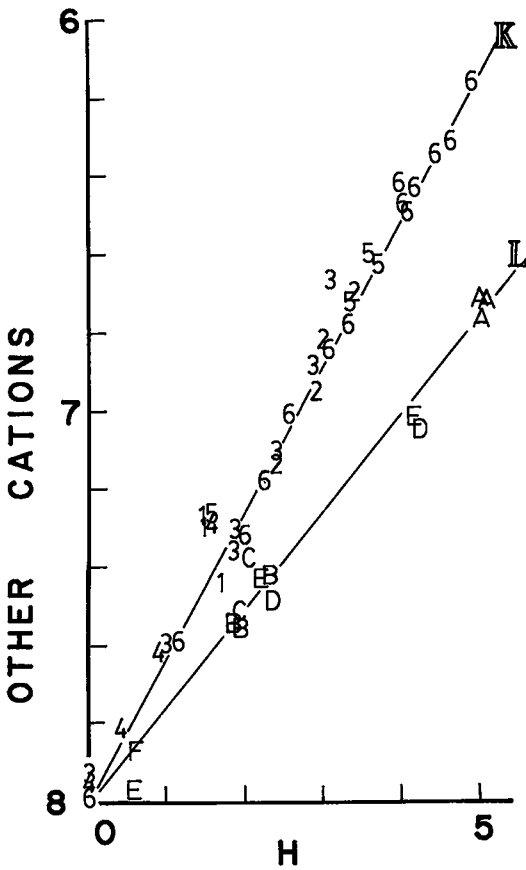


FIG. 3. Scatter diagram of cation content (except hydrogen) versus hydrogen content (number of cations) of hydrogarnet samples, calculated for 12 oxygen atoms. Water is calculated by difference. Symbols: A HG1, B HG2, C Manning & Owens (1977), D Hutton (1943), E Deer *et al.* (1962, p. 105), F Peters (1965), 1 SC1, 2 SC2, 3 76162, 4 76168, 5 77398, 6 77399.

difference in OH in these two samples (*cf.* Hsu 1980, p. 412). In contrast to the hydrogrossular samples, hydrogarnet 77399 shows very different Si-O absorption bands (1075, 1025, 545, 480 cm^{-1}). The spectrum for hydrogarnet reported here is also different from that reported by Hsu (1980), who illustrated a spectrum for synthetic hydrossessartine that is virtually identical to that for his synthetic hydrogrossular.

DERIVATION OF THE HYDROGARNET FORMULA

The formula for hydrogarnet is derived from the microprobe analyses, with the difference from 100% taken as representing H_2O . That the hydrogarnet compositions cannot be reconciled with a hydrogrossular-type formula is illustrated in Figure

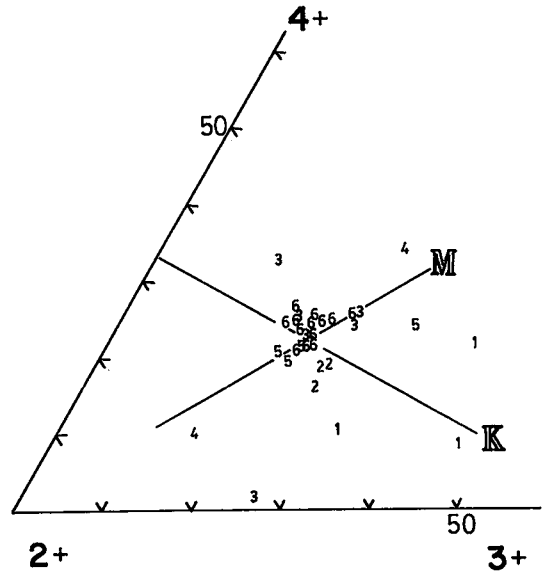


FIG. 4. Relative numbers of cationic vacancies in hydrogarnet. Line K is transferred from Figure 3, line M illustrates $R^{4+}:R^{3+} = 1:1$ substitution by H. Symbols as in Figure 3.

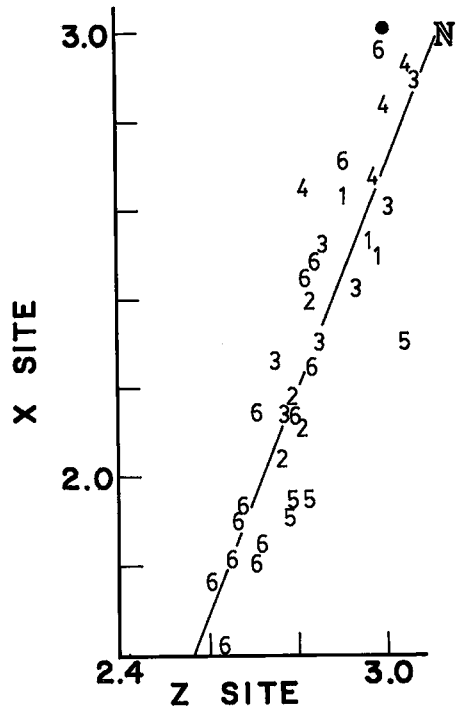
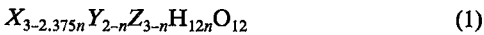


FIG. 5. Populations of the X and Z sites for hydrogarnet, where Fe^{3+} is calculated to fill the octahedral site. Line N is a least-squares regression, slope 2.52. Other symbols as in Figure 3.

3. Line L in Figure 3, of apparent slope 0.25, is the predicted distribution of hydrogrossular compositions based on the formula $X_3Y_2Z_{3-n}H_{4n}O_{12}$ (symbols from Meagher 1980). HG1, HG2, and other hydrogrossular compositions from the literature are well described by this line. Line K, of apparent slope 0.375 (close to a least-squares regression line of slope 0.373) is chosen to describe the distribution of hydrogarnet compositions in Figure 3. Changing some Fe^{2+} to Fe^{3+} and reducing the calculated H_2O content do not bring the observed compositions of hydrogarnet nearer the hydrogrossular line.

Based on the relative number of ions "missing" from the three types of cationic sites in the garnet structure, as illustrated in Figure 4, charge-balance considerations and scaling the substitution to the H in the tetrahedral site (to correspond to the presentation of the hydrogrossular formula), the hydrogarnet formula can be expressed as



Inspection of the electron-probe data shows that sufficient cations are available to fill the octahedral site by converting some Fe^{2+} to Fe^{3+} . There always is sufficient Fe available to fill the octahedral site; no Mn^{3+} is required. For computational purposes, Fe or Mn could be used to fill the octahedral site, as the precision of the analyses would not separate the two cases. A hydrogarnet formula calculated using the relative numbers of 'missing' cations, as illustrated in Figure 5 using line N, of slope 2.5 (close to a least-squares-regression slope of 2.52), is



The true hydrospessartine formula probably lies between the two extreme formulae calculated here, and may vary for different samples.

Recalculating the garnet compositions to fill the octahedral site with Fe^{3+} causes considerable variation in the ratio of ferric to ferrous ions in the composition of individual samples. Normally, variations of this sort would make the proposed formula suspect. The regularity of the calculated Fe^{2+}/Fe^{3+} ratios as a function of Mn, however, suggests that there is a basis for this treatment (Fig. 6). It is further to be remarked that the data points in Figure 5 show considerably less scatter than the points in analogous diagrams drawn without filling of the octahedral site.

DISCUSSION

What controls the site selection of hydrogen in the garnet structure? Natural hydrogrossular and synthetic garnet are associated with low-silica environments (rodingites, pyroxenites, plastic beakers; Ito

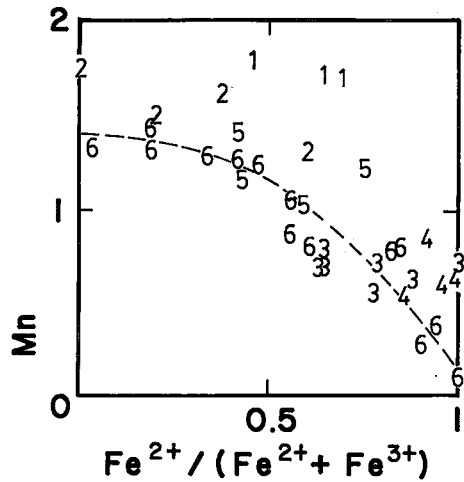


FIG. 6. Number of Mn cations per 12 oxygens atoms versus calculated $Fe^{2+}/(Fe^{2+} + Fe^{3+})$, where the octahedral site is filled with ferric iron in hydrogarnet samples. Symbols as in Figure 3.

& Frondel 1967). The hydrogarnet samples reported here all coexist with quartz. We suggest that in silica-saturated environments, hydrogen can compete for and enter garnet sites other than the tetrahedral site.

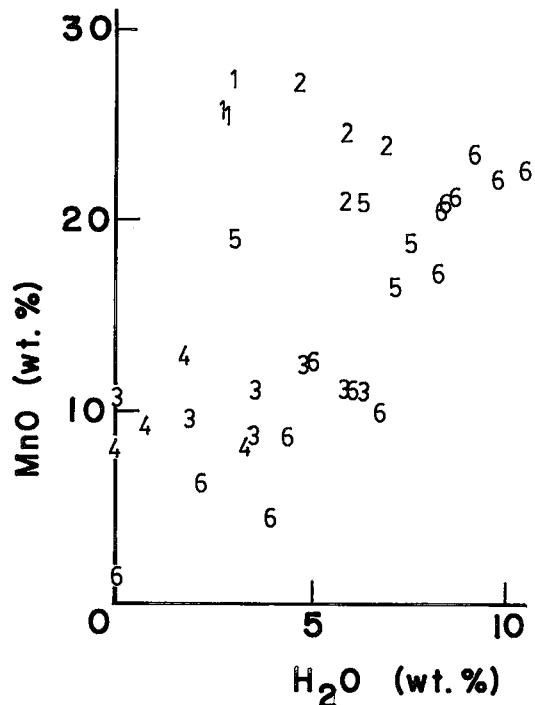


FIG. 7. Scatter diagram of MnO versus inferred H_2O in hydrogarnet. Symbols as in Figure 3.

Although Hsu (1980) has carried out preliminary experiments under silica-saturated conditions, the microprobe data required to test this hypothesis have not been reported.

What controls the extent of hydrogen substitution in hydrogarnet? Examination of the electron-microprobe data indicates that none of CaO, Fe₂O₃ (calculated) nor MnO (Fig. 7) is directly correlated with H₂O calculated by difference. Three of the six samples studied contain garnet grains zoned to apparently anhydrous compositions. Hydrogen zoning in hydrogarnet may be associated with (a) a narrow stability-field, in terms of temperature, of hydrogarnet showing solid solution toward an anhydrous garnet, (b) growth of the garnet in a migrating or ephemeral fluid phase during a prograde metamorphic reaction with decreasing P(H₂O) as the reaction proceeds, or (c) an as yet unrecognized control on hydrogen uptake by some other component or combination of components.

As a mineral of low-grade metamorphic rocks, associated with phases now receiving attention in thermodynamic studies (e.g., Ferry 1980), hydrogarnet is worthy of more attention. As it is a silicate of reasonably common occurrence showing hydrogen zoning, careful characterization of hydrogarnet in future studies may lead to improved understanding of the thermodynamics of Si and H in metamorphic rocks and fluids (H. Greenwood, pers. comm. 1979). Better understanding of hydrogarnet may lead to improved geothermometers for garnet-bearing low- and medium-grade metamorphic rocks.

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