

## The hydrous component in garnets: pyralspites

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### Abstract

Natural pyralspite garnets have been found to commonly contain a hydrous component, ranging in concentration from 0.02 to 0.25 wt.% as H<sub>2</sub>O. Anhydrous pyralspites of crustal origin are rare. Of forty crustal garnets examined, only two were anhydrous. The most-hydrous garnets were spessartines from igneous pegmatites. Metamorphic garnets had lower water contents, and frequently also contained hydrous inclusions. The infrared absorptions of the hydrous component in the garnet end members are characteristic, and consist of 2 to 4 narrow bands centered at 3640 cm<sup>-1</sup> in spessartine, 3500 cm<sup>-1</sup> in almandine, and 3670 cm<sup>-1</sup> in pyrope. The IR spectra indicate that the hydrous component is not in the form of molecular H<sub>2</sub>O; the most likely form is H<sub>4</sub>O<sub>4</sub><sup>4-</sup> substituting for SiO<sub>4</sub><sup>4-</sup> but other substitutions involving multiple OH<sup>-</sup> groups on one site are consistent with the data. The concentration of OH (as H<sub>2</sub>O) in garnets may be determined from the integral absorptivity (K) in the 3700–3400 cm<sup>-1</sup> region, although K varies with chemistry from 3700–6000 (1 mol<sub>H<sub>2</sub>O</sub><sup>-1</sup> cm<sup>-2</sup>) in end members to 120–600 in intermediate compositions.

### Introduction

The hydrous component found in many garnets is routinely ascribed to the hydrogarnet substitution, H<sub>4</sub>O<sub>4</sub><sup>4-</sup> ⇌ SiO<sub>4</sub><sup>4-</sup>. The characteristics of this substitution are poorly defined in natural garnets, however. This is particularly true of the pyralspite garnets, the pyrope–almandine–spessartine series. In this paper we discuss the nature and extent of the hydrous component commonly found in pyralspite garnets. In a forthcoming paper, we will discuss the grandite series. These papers address the questions of the degree to which all natural garnets may be expected to contain a hydrous component, and whether that hydrous component is the classic hydrogarnet substitution, other substitutional hydroxide, molecular water or fluid inclusions, or alteration and included hydrous phases. Previous studies have concentrated on rare garnets containing 1% H<sub>2</sub>O or more; we have instead concentrated on understanding the hydrous component in common garnets.

Hydrogarnets were first described by Cornu (1906) and Foshag (1920). Winchell (1933), Flint et al. (1941), Pabst (1937, 1942), and Belyankin and Petrov (1941) brought understanding of the natural hydrogarnets to the point where it was realized that the H<sub>4</sub>O<sub>4</sub><sup>4-</sup> ⇌ SiO<sub>4</sub><sup>4-</sup> substitu-

tion accounted for the chemistries of hydrous grandites known at that time. Modern research has focused almost exclusively on synthetic hydrogrossular. A series of papers by Cohen-Addad and co-workers proved, using neutron diffraction and other techniques, that in several synthetic compounds including hydrogrossular there are, in fact, tetrahedral groups of 4OH<sup>-</sup> replacing the SiO<sub>4</sub><sup>4-</sup> tetrahedron (Cohen-Addad et al., 1964, 1967; Cohen-Addad 1968, 1969). These results were confirmed by Foreman (1968). There are, however, no direct determinations of the H<sub>4</sub>O<sub>4</sub> tetrahedral grouping in natural garnets. The proton positions in hydrogarnet type substitutions have only been verified by neutron diffraction in natural materials in henritermierite (Aubry et al., 1969), and by X-ray diffraction in bicchulite (Sahl, 1980) and zunyite (Baumer et al., 1974).

The pyralspite series is not well known for containing a hydrous component. Ackermann et al. (1983) describe the synthesis of hydrous pyropes, which they assume contain the hydrogarnet substitution. Wilkins and Sabine (1973) reported that two spessartines from Sterling Hill, New Jersey, contained up to 2.5 wt.% H<sub>2</sub>O. Hsu (1980) synthesized hydrospeessartine, but the garnets were reported to be metastable.

In this paper we discuss the extent to which natural pyralspite garnets contain a hydrous component, and the evidence for the speciation of that component. The hydrogarnet substitution (H<sub>4</sub>O<sub>4</sub><sup>4-</sup> ⇌ SiO<sub>4</sub><sup>4-</sup>), or other substitutional hydroxides would constitute a structural hydrous component. They are part of the crystal struc-

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ture and their properties are linked to those of the basic garnet structure. Other forms for a hydrous component are basically inclusions of a foreign phase: fluid inclusions, alteration, or included hydrous phases. Regardless of the actual speciation, we report the content of hydrous component as  $H_2O$  because that is the species actually measured by our analytical methods. We have tabulated the total amounts of  $H_2O$  present in pyralspites from a variety of occurrences and localities, and determined calibrations for structural  $H_2O$  content in pyralspites. The major tool used in this study was infrared (IR) spectroscopy, because of its sensitivity to the O-H bond. The use of IR spectroscopy to determine the speciation of trace hydrous components in minerals is discussed by Aines and Rossman, (1984a). Water contents were obtained from infrared integral absorptivity, calibrated by thermogravimetry,  $P_2O_5$  cell coulometry, and  $H_2$  gas manometry.

### Methods

Infrared spectra were obtained on doubly polished, single crystal slabs of garnet, using techniques described by Goldman et al. (1977). A Perkin-Elmer model 180 grating infrared spectrometer was used for both room temperature and cryogenic measurements. Near infrared (NIR) measurements were obtained using a Cary 171 grating spectrometer. IR spectra were recorded digitally using an interface with a DEC MINC-11 computer. These spectra were corrected for baseline and then used to determine integrated areas under absorption bands.

Water contents were calculated by calibrating the integrated IR intensities against the water content measured with a DuPont moisture evolution analyzer (MEA). Reagent grade  $Mg(OH)_2$  was used as a standard material; its water content was calibrated using thermogravimetry. The carrier gas used was  $N_2$  or 99%  $N_2$ :1%  $O_2$  for samples containing ferrous iron. In these samples it is possible for  $H_2O$  to oxidize the iron, evolving  $H_2$  gas which is not detected by the cell. The oxygen gas is added to react with  $H_2$  to regenerate  $H_2O$  prior to reaching the electrolytic cell.

100 to 200 mg of coarsely powdered garnet was used for MEA analysis. Samples were held at  $110^\circ C$  until no more moisture was measurable, then heated at  $\sim 500^\circ$ /minute to  $1000^\circ C$ . The moisture evolved was taken as the water content of the garnets. The blank for this technique is  $30 \pm 10 \mu g H_2O$ , as determined from empty boat runs, and runs using identically prepared anhydrous garnet. The precision is approximately 5% of the measurement (exclusive of the error in the blank) as measured using the  $Mg(OH)_2$  standard. The primary errors in this measurement are due to adsorbed water on furnace walls and tightly bound water on particle surfaces that was added during grinding. The water added during grinding ranged up to 0.04 wt.%. It was kept below 0.02% for the analyses reported here by thoroughly drying the mortar and pestle

in a vacuum oven at  $160^\circ C$  and by not overgrinding the samples. The average particle size was  $25 \mu m$ .

Water contents were also estimated by thermal gravimetric analysis using a Mettler TA2000 TGA system. The lower detection limit is  $\sim 100 \mu g$  with a precision of approximately  $\pm 50 \mu g$ . Up to 100 mg of powdered sample was used per run. The primary error in this measurement is due to buoyancy changes in the sample during the course of the run, which is made with constant flow of  $N_2$  gas. Measurements were made up to  $1200^\circ C$ .

Samples 13 and 49 were analyzed by gas volumetric methods. 500 mg of the powdered samples were heated to  $1400^\circ$  and the evolved gas was converted to  $H_2$ , then measured manometrically. This analysis was performed in James O'Neil's laboratory at the USGS, Menlo Park, California, facility.

Major element analyses were performed using the Caltech MAC5 automated microprobe, with data reduction methods described by Bence and Albee (1968) and the alpha factors of Albee and Ray (1970). A pyrope collected by T. McGetchin from the Moses Rock diatreme, Utah, was used as a secondary standard (Champion et al., 1975). This garnet is homogeneous and has been extensively used as a microprobe secondary standard. It is included in Table 1, Sample #110. In no instance was there sufficient  $H_2O$  in these garnets for the microprobe analyses to be significantly silica deficient.

### Samples

A total of 75 pyralspite garnets were surveyed for the presence of a hydrous component. A summary of the localities and occurrences of samples that were analyzed in detail is given in Table 1. The garnets were museum specimens, and details of associated phases can not be obtained directly. Table 1 contains references to the detailed petrology of the localities, where available. Only representative samples from several diatreme and kimberlite localities are listed in Table 1. A more complete discussion of the hydrous mantle garnets encountered during the course of this project will be published later. Samples were chosen to represent the common range of natural chemistries of pyralspite garnets, to represent the common occurrences, and to be a sufficient size (and lacking inclusions) for accurate analysis.

The necessary size of gemmy material is approximately  $250 \mu m$  in diameter by 1 mm in thickness for spectroscopic analysis. More material is required for the analytical techniques used for  $H_2O$  concentration. Accordingly, analytical results on large samples were used to calibrate the infrared integral absorptivity so that water contents could be measured on extremely small samples. The effects of inclusions on spectroscopic results were determined by studying samples which contained zones of high and low inclusion content. All samples were doubly polished for IR analysis, and the same sample was then analyzed by microprobe utilizing the existing polished surface.

Table 1. Localities and occurrences of garnets used in this study

Sample Number	Locality	Type	Occurrence, Comments	Caltech Number	Reference
2	Minas Gerais, Brazil	Spess	Igneous pegmatite	7765	
4	Rutherford #2, Amelia, Va	Spess	Igneous pegmatite	6725	Sinkankas, 1968
5	Rutherford #2, Amelia, Va	Alm-Spess	Igneous pegmatite	6725	Sinkankas, 1968
10	Tanzania	Spess-Alm		15001	
11	Unknown, East Africa (?)	Py-Alm		15002	
12	Minas Gerais, Brazil	Spess-Alm	Igneous pegmatite (?)	15003	
13	Asbestos, Quebec	Gross	Altered ultramafic body	15004	Grice & Williams, 1979
19	Franklin, N. Jersey	Gross-Spess		N.M.N.H.#11318*	Frondel, 1972
21	Unknown	Py-Alm		15005	
22	Brazil	Alm-Spess		15006	
23	Wrangell, Alaska	Alm	Metamorphic, schist	15007	Sinkankas, 1976
27	Spruce Pine, N. Car.	Spess-Alm	Igneous pegmatite. Zoned.	1738	Parker, 1952
28			Other zones in Sample 27;		
29			27 rim, 28 middle, 29 core		
32	Rincon, Calif.	Spess-Alm	Igneous pegmatite	15008	Jahns & Wright, 1951
33	Mt. San Jacinto, Calif.	Alm	Xenolith in tonalite	9968	Hill, 1984
34	Ugelvik, Norway	Py	Ultramafic body	15009	Carswell, 1968
35	Gore Mt. New York	Alm-Pyr	Metamorphic gneiss	15010	Levin, 1950
49	Green Knobs, N. Mex.	Py	Diatreme megacryst	15011	Smith & Levy, 1976
55	Anakapelle, India	Py-Alm	Metamorphic, granulite	Ed Grew #3080L	Grew, 1982
56	Casey Bay, Antarctica	Py-Alm	Metamorphic, granulite	Ed Grew #2434E	Grew, 1981
57	North River, N. York	Py-Alm	Metamorphic, granulite	10244	Levin, 1950
61	Garnet Ridge, Ariz.	Py-Alm	Diatreme megacryst	15013	Hunter & Smith, 1981; Switzer, 1977
64	Garnet Ridge, Ariz.	Py	Diatreme megacryst	15013	Hunter & Smith, 1981; Switzer, 1977
65	Garnet Ridge, Ariz.	Py-Alm	Diatreme megacryst	15013	Hunter & Smith, 1981; Switzer, 1977
78	Minas Gerais, Brazil	Spess	Igneous pegmatite (?)	15014	
89	Wesselson Mine, S. Afr.	Py	Kimberlite megacryst	Harvard #12528	
95	Roberts Victor Mine, South Africa	Gross-Py	Kyanite bearing eclogite nodule	N.M.N.H.#87375	
104	Rock Mica Mine, Yancey Co., N. Car.	Alm-Spess	Igneous pegmatite	1731	Parker, 1952
105	Broken Hill, Australia	Alm-Spess		11826	
110	Moses Rock, Utah	Py	Diatreme megacryst	15016	McGetchin & Silver, 1972
111	Chanthaburi, Thailand	Alm-Py	Nodules in alkali basalt	9964	
112	Podsedice, Czech.	Py		15017	Hintze, 1897, p. 63
113	Garnet Ridge, Ariz.	Py	Diatreme	15013	Hunter & Smith, 1981; Switzer, 1977
114	Garnet Ridge, Ariz.	Py	Diatreme	15013	Hunter & Smith, 1981; Switzer, 1977
118	St. Lawrence, N. York	Alm	Metamorphic, granulite	15012	Levin, 1950

\*National Museum of Natural History.

## Results

Forty pyralspite garnets of crustal origin were studied; all but two were hydrous, as indicated by the presence of absorption bands in the 3400 to 3700  $\text{cm}^{-1}$  region. Peaks in this region are typical of O-H stretching absorptions (e.g., Aines and Rossman, 1984a). Typical "water" contents are 0.1 wt.%, ranging up to 0.25 wt.%. This hydrous component is structural, not due to inclusions or alteration which may considerably increase the apparent water content. Pyralspites of mantle origin are also frequently hydrous.

Figures 1 and 2 show the major element chemistry of the garnets studied and the integrated IR absorptivity due to structural hydrous component. Water contents may be calculated from integrated IR absorption as shown in the scale bar in Figure 1 which was calibrated using MEA and TG results. Only the concentration of structural hydrous component is shown in Figures 1 and 2. Some samples also contained hydrous inclusions or were altered and the relative amount of water held in structural versus non-structural sites could not be determined. These are shown as squares containing a cross in Figures 1 and 2. Samples that were badly altered, largely metamorphic garnets, are not included in these figures. The pyrope-almandine and spessartine-almandine series are plotted against grossular

because most pyralspites contain some calcium. In many respects it is appropriate to consider the octahedral  $\text{Al}^{3+}$  garnets (pyrope, almandine, spessartine, grossular) as a single group. One representative end-member grossular is included in Table 1. A discussion of the grossular-andradite series is in preparation.

### "Water" contents

Figures 1 and 2 show the content of hydrous component in the garnets studied in terms of integrated infrared absorption measured from 3750  $\text{cm}^{-1}$  to 3400  $\text{cm}^{-1}$ . This method of measuring the hydrous component is very sensitive, limited only by the sample thickness available, but must be calibrated by another method in order to obtain absolute "H<sub>2</sub>O" concentrations. The primary calibration method used was P<sub>2</sub>O<sub>5</sub> cell coulometry using the moisture evolution analyzer. Table 2 shows the results of MEA calibration of the IR integrated absorbance. Samples listed here were analyzed first by IR, then ground for MEA. The strong zoning present in some samples (for example up to a factor of 10 for points separated by 4 mm in sample numbers 27-29) required that the same area used for IR be powdered for MEA.

The result of primary interest in Table 2 is the large variation in integral molar absorptivity seen between end-member and intermediate-chemistry garnets. Spessartine

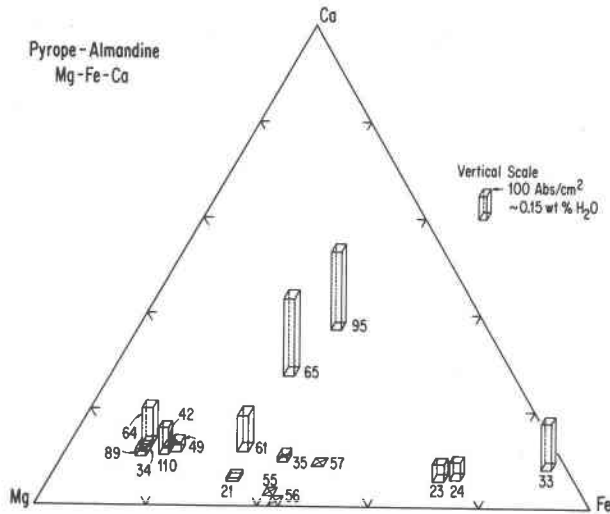


Fig. 1. Chemistries and "water" contents of pyrope-almandine garnets studied. Cation contents are plotted as mole %. None of the garnets deviate significantly from  $M_3^{2+}Al_2Si_3O_{12}$ ,  $M = Ca, Mg, Fe$ . The vertical axis is integral infrared absorbance in the region  $3750$  to  $3400\text{ cm}^{-1}$ , which is related to water content as shown in the scale and in Table 2. Squares with no vertical extension and which are filled with a cross represent samples that were too badly altered to determine the content of structural hydrous component, even though the IR pattern indicated that one was present. Sample numbers refer to Table 1.

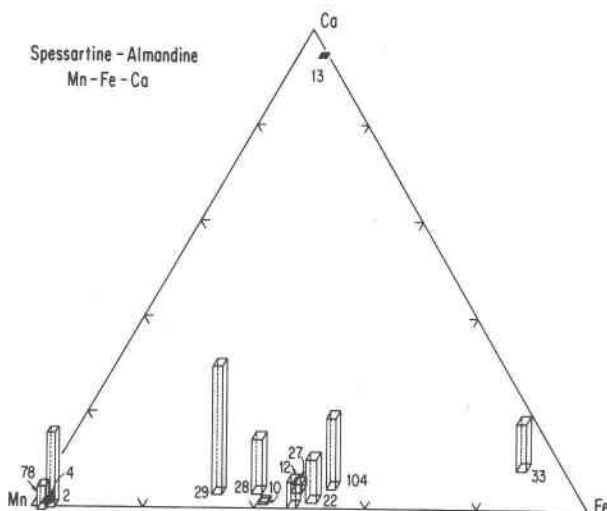


Fig. 2. Chemistries and "water" contents of spessartine-almandine garnets studied. Same scale as Fig. 1. None of these samples differs significantly from  $M_3^{2+}Al_2Si_3O_{12}$ ,  $M = Mn, Fe, Ca$ . Vertical extension has not been shown for samples 4 and 13, which have very large integral absorbances due to the large molar absorptivity of these end member garnets; their water contents are similar to those of the other samples (see Table 2).

Table 2. Integral molar extinction coefficients

Sample Number	H <sub>2</sub> O* (wt%)	K# (liter mol <sup>-1</sup> cm <sup>-2</sup> )	Composition (mole %)
2	0.084 ± 0.04	3700	Mn <sub>97</sub>
4 ##	0.25 ± 0.01	5900	Mn <sub>97</sub>
5	0.36 ± 0.02	5820	Mn <sub>95</sub>
10	0.059 ± 0.03	116	Mn <sub>60</sub> Fe <sub>40</sub>
12 ##	0.17 ± 0.02	620	Mn <sub>55</sub> Fe <sub>45</sub>
13 ##	0.18 ± 0.01 **	8000	Ca <sub>97</sub>
35	0.06 ± 0.01	180	Mg <sub>45</sub> Fe <sub>55</sub>
49	0.08 ± 0.02 **	260	Mg <sub>75</sub> Fe <sub>25</sub>
104	0.27 ± 0.02	1103	Mn <sub>45</sub> Fe <sub>55</sub>
113 ##	0.15 ± 0.03	340	Mg <sub>75</sub> Fe <sub>25</sub>
114	0.22 ± 0.03	320	Mg <sub>75</sub> Fe <sub>25</sub>

\* Determined by MEA analysis. Errors based on duplicate measurements and known error in MEA measurement which is largely a function of the amount of sample available.

\*\* Determined by H<sub>2</sub> gas volume. For Sample 13, MEA gave identical results. No MEA available for Sample 49.

# Determined from integral absorption from  $3750$  to  $3400\text{ cm}^{-1}$ .

## These samples were checked for complete dehydration at  $1000^\circ\text{C}$  by heating a slab in air for four hours. All lost at least 95% of their original IR intensity.

and grossular have a molar absorptivity ( $K$ ) of around  $5000$  to  $6000$  ( $l\text{ mole}^{-1}\text{ cm}^{-2}$ ) while the spessartine-almandines and pyrope-almandines have absorptivities of  $200$  to  $500$ . Some of the variability seen in Table 2 may be ascribed to analytical error. Major sources of error include alteration in the sample and surface hydroxyl which forms during grinding even in a low humidity atmosphere. This averaged  $0.02$  to  $0.04\text{ wt.}\%$ . These problems may account for the variability among each group, but the extreme difference between the end-members and intermediate chemistries is considerably larger than any possible error.

Two of the samples in Table 2 were analyzed by the H<sub>2</sub> gas volume technique. Sample 49 was not analyzed by MEA because of small sample size. Sample 13 was analyzed by both techniques and both gave identical results within error: MEA (two analyses)  $0.18\%$  ( $\pm 0.01$ ); H<sub>2</sub> gas  $0.17\%$  ( $\pm 0.02$ ). Sample 13 is from the same locality as the material used by Westrum, et al. (1979) in a study of the thermophysical properties of grossular. They obtained a water content of  $0.19\text{ wt.}\%$ . Several samples were also measured using thermogravimetry. The errors due to buoyancy for small samples were considerably larger than the corrected weight losses, and all samples studied in this way gave considerably greater weight losses than indicated by MEA. Sample 13, for instance, lost  $0.53\text{ wt.}\%$  from  $100$  to  $1100^\circ\text{C}$ . The sample weighed  $112\text{ mg}$ . Considerably larger samples are required for accurate TG work, and no single sample was large enough. An average sample of  $500$  purple and red garnets from the Garnet Ridge, Arizona, diatreme was ground and sieved to pass  $200$  mesh but not pass  $325$  mesh. In this

way a 1-gram sample was available for TG, and it yielded a weight loss of 0.14%. The same sample gave an MEA result of 0.12%, confirming that the values in Table 2 are not artifacts of small sample size. Individual garnets from the same locality yielded from 0 to 0.22 wt.% H<sub>2</sub>O by MEA, in accord with their integrated IR absorbances (Table 2).

The complete dehydration of the garnets measured by MEA was verified in four cases (Table 2) by heating a doubly polished slab at 1000°C for four hours. All four showed greater than a 95% loss of integrated intensity in the infrared spectrum of the O–H region after this treatment, indicating that the MEA analysis at 1000°C is valid. TG curves for single samples and the 500-stone average Garnet Ridge sample show continuous weight loss from 200° to 1000° when heated at 5°C/min. The structural hydrous component in pyralspites is not stable to very high temperatures, if at all, at  $P_{\text{tot}} = 1$  bar.

### Infrared analysis

IR spectroscopy was used to determine the nature of the hydrous component, if present, and to calculate the total water content from the integral absorption intensity.

**End-members.** The IR absorption patterns for typical end-members of the octahedral Al<sup>3+</sup> garnets are shown in Figure 3. Only the grossular and spessartine are true end-members. The pyrope and almandine both contain ~20 mol% of almandine and pyrope component, respectively. The examples shown in Figure 3 are all gemmy crystals with no hydrous inclusions or alteration.

Two important results of the infrared analysis of pyralspites are exhibited in Figure 3. (1) End member patterns are composed of multiple absorption peaks. (2) The location of the center of the multiple peaks varies with the chemistry. The grossular and spessartine end-member patterns are best known since multiple examples of them were available. All end-member grossulars and spessartines studied have IR spectra similar to those in Figure 3. The multiple peaks in almandine are not as well-resolved as those in grossular and spessartine. All pyropic garnets studied have patterns similar to that seen in Figure 3, but as discussed below this is probably not an end-member spectrum. The end-member pyrope pattern is not well determined because of the absence of stoichiometric pyropes in nature and the low water content of common Mg<sup>2+</sup>-rich garnets.

The spectra shown in Figure 3 were obtained at –196°C to enhance the separation between peaks. At room temperature the spectra differ only in appearing less well resolved; all the peaks may be identified but may occur as shoulders rather than distinct peaks. The spectra in Figure 3, as well as the other spectra in this paper, have been corrected to remove the effects of a broad Fe<sup>2+</sup> absorption centered at 4240 cm<sup>-1</sup>. The Fe<sup>2+</sup> absorption produces a strongly sloping background which was re-

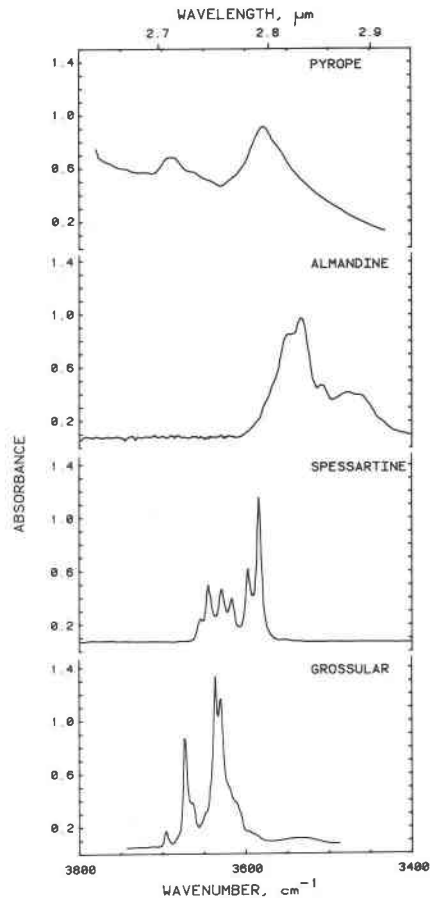


Fig. 3. Typical single crystal infrared spectra of end-member pyralspite garnets obtained at –196°C. From bottom to top: grossular, sample 13, 0.14 mm thick; spessartine, sample 14, 0.06 mm thick; almandine, sample 23, plotted as 11.0 mm thick; pyrope, sample 49, plotted as 10.0 mm thick. End-member hydrous garnets of these chemistries always give IR patterns like these with the exception of the peaks shown here of absorbance less than 0.2, which are not reproducible and are due to inclusions or alteration. These spectra have been corrected for a sloping baseline due to an Fe<sup>2+</sup> electronic absorption at 4200 cm<sup>-1</sup>, with the exception of the pyrope which is uncorrected to show the baseline. In the absence of a hydrous component, all garnets are featureless in the 3700–3400 cm<sup>-1</sup> region.

moved using a scaled baseline obtained from a rigorously anhydrous garnet, sample #111.

The consistent nature of the IR spectra of the end-member pyralspites is striking. No exceptions to this behavior were observed in this study; if end-member garnets were hydrous, they gave the IR spectra seen in Figure 3. This is strong evidence that the absorption pattern is intrinsic to garnet rather than from an alteration product or included phase. In other words, there is a structural hydrous component in natural pyralspites

**Alteration.** Many pyralspites contain a hydrous component that is clearly not structural and, in fact, is not part

of the garnet but rather part of an included phase. Water of this type may be recognized by two methods. (1) In garnets with varying concentrations of inclusions or altered regions, any component of the IR spectrum that changes from region to region in the same manner as the inclusion concentration is assumed to be due to the alteration or included phases. (2) Any component of the IR spectrum of a garnet that is inconsistent with the spectra expected for a garnet of that chemistry is assumed to be due to alteration. Criterion (2) could only be applied after many garnets were studied and the patterns of spectral behavior were established.

Figure 4 shows how these criteria are applied to two actual cases. The top two spectra are of an almandine from Wrangell, Alaska. The upper trace is in a region of many inclusions, some of which appear to be chlorite, based on microprobe analysis. Below that is a spectrum of an inclusion-free, gemmy region of the crystal. Identical spectra are obtained in all inclusion-free portions of this crystal. The intrinsic, structural hydrous component

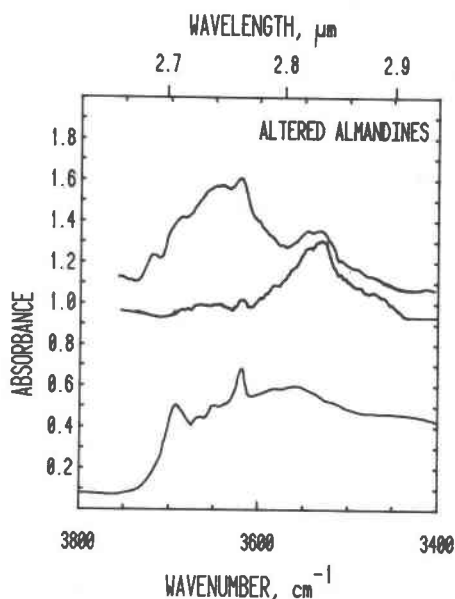


Fig. 4. Example of two altered almandine garnets showing the spectral features which allow alteration and inclusions to be distinguished from a structural hydrous component. The upper two traces are both from a single crystal of sample 23. The uppermost trace shows a region of inclusions, the lower trace a gemmy area which gives a typical pattern for almandine structural hydrous component. The peaks in the upper trace in the 3700–3600  $\text{cm}^{-1}$  region are due to the inclusions or alteration. The sample is plotted as 3.8 mm thick. The lowermost trace shows a 0.7 mm thick almandine from a granulite, sample 118. The extremely broad band underlying the sharp peaks is characteristic of incipient alteration. It extends to 3000  $\text{cm}^{-1}$ . All three of these spectra have a sharp peak at 3625  $\text{cm}^{-1}$  which is the characteristic O–H stretching frequency of muscovite, and may be attributed to muscovite inclusions.

in this garnet gives rise to the peak at 3550  $\text{cm}^{-1}$ , a peak seen in other almandines, while the higher wavenumber peaks are due to included hydrous phases. The lowest spectrum in Figure 4 is of a spessartine–almandine garnet in which there is incipient alteration. The extremely broad band ( $\sim 400 \text{ cm}^{-1}$  in width) seen underlying the sharper peaks is characteristic of incipient alteration in which crystallites have not yet formed. It is similar to the spectra seen for fluid inclusions (Aines and Rossman, 1984a). This garnet has obvious cloudy zones of alteration extending several hundred micrometers inward from large cracks.

*Intermediate chemistries.* The spectral patterns of the intermediate composition pyralspites are more complex than those of the end-members. Once alteration and included phases are removed from consideration, two common factors are seen in the behavior of the intermediate garnets. (1) Multiple peaks occur, and (2) sharp bands of the sort seen in Figure 3 do not occur. The sharpest peaks seen in end-member spessartine are  $\sim 10 \text{ cm}^{-1}$  in width (at half height) while the sharpest bands seen in intermediate compositions are 40–50  $\text{cm}^{-1}$  wide, as broad as the entire set of sharp bands seen in the end-members.

Figure 5 shows the infrared spectra of typical members of the spessartine–almandine series. The chemistries of these samples are shown in Figure 2. Although the spectra of the intermediate compositions are complex, they appear to be simple combinations of the end-member patterns. The broad bands of the intermediate compositions appear to be averaged versions of the multiple sharp bands seen in the end-members as, for instance, the two most spessartine-rich samples at the top of Figure 5.

Despite a consistency of spectral behavior in the  $\text{Mn}^{2+}$ – $\text{Fe}^{2+}$  series, the transition between spectral patterns is not entirely a smooth function of chemistry.  $\text{Mn}^{2+}$ -rich samples are always dominated by the bands at  $\sim 3640 \text{ cm}^{-1}$  and  $\sim 3600 \text{ cm}^{-1}$ , and  $\text{Fe}^{2+}$  garnets are dominated by the bands at  $\sim 3470 \text{ cm}^{-1}$  and  $\sim 3540 \text{ cm}^{-1}$ . However, as seen in the  $\text{Mn}^{2+}$ -rich samples of Figure 5 (the top two), the relative intensities of the 3640  $\text{cm}^{-1}$  and 3600  $\text{cm}^{-1}$  bands may vary widely. This behavior is also seen for the  $\text{Fe}^{2+}$ -related peaks at  $\sim 3470 \text{ cm}^{-1}$  and 3540  $\text{cm}^{-1}$ . Several spessartines of near end-member chemistry contain minor peaks in the region observed for  $\text{Fe}^{2+}$ -related peaks. (These samples contain lamellar bands,  $\sim 200 \mu\text{m}$  across, that are slightly more brown than the bulk sample.) The consistent peak locations and slightly variable peak intensities suggest that there is a structural hydrous substitution present, but that factors other than the bulk chemistry may control the extent or structure of the substitution.

Similar behavior is seen in the  $\text{Mg}^{2+}$ – $\text{Fe}^{2+}$  series (Fig. 6), but the smooth progression of spectral pattern with chemistry seen in Figure 5 is not present. Again, there are four fundamental bands, and the high wavenumber pair at  $\sim 3660 \text{ cm}^{-1}$  and  $3560 \text{ cm}^{-1}$  are associated with  $\text{Mg}^{2+}$ -rich garnets, and the low wavenumber pair at 3470  $\text{cm}^{-1}$  and

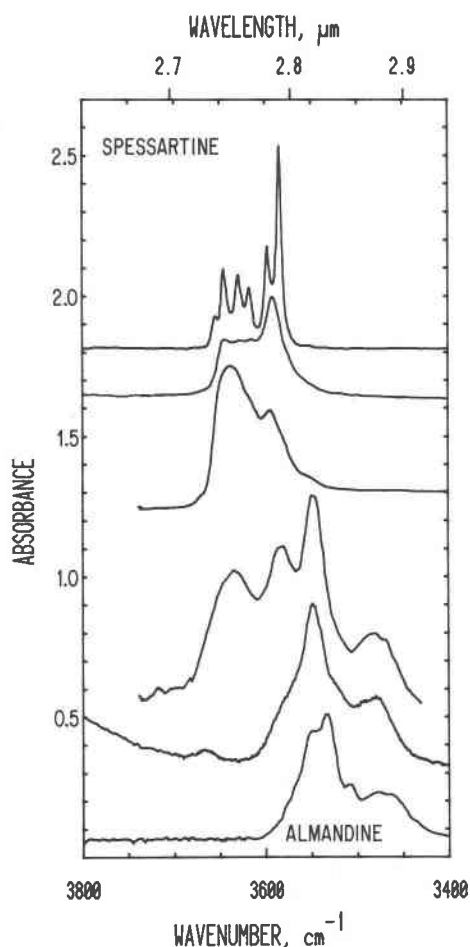


Fig. 5. Infrared spectra of typical members of the spessartine-almandine series showing the progression of spectral patterns at intermediate chemistries. From bottom to top: sample 23, plotted as 5.5 mm; sample 104, plotted as 1.8 mm; sample 27, plotted as 13 mm; sample 29, plotted as 0.7 mm; sample 5, 0.06 mm thick, and sample 4, 0.06 mm thick. All spectra recorded at  $-196^{\circ}\text{C}$ .

$3540\text{ cm}^{-1}$  are associated with  $\text{Fe}^{2+}$ -rich garnets. At the intermediate chemistries (middle trace of Fig. 6), however, the highest and lowest wavenumber bands are greatly diminished in intensity. The IR pattern is dominated by a band that appears to be a combination of the  $3560\text{ cm}^{-1}$  and  $3540\text{ cm}^{-1}$  bands.

**Near infrared spectroscopy.** The  $5200\text{ cm}^{-1}$  overtone band of molecular water allows one to distinguish between molecular  $\text{H}_2\text{O}$  and  $\text{OH}^-$  ions. This band arises from combined bending and stretching, and cannot occur for  $\text{OH}^-$  ion (e.g., Aines and Rossman, 1984a). Figure 7 shows the near infrared (NIR) spectrum of a hydrous spessartine. Superimposed upon three broad bands ( $\sim 1000\text{ cm}^{-1}$  wide) are a number of sharp bands ( $\sim 20\text{ cm}^{-1}$  wide). The broad bands are electronic transitions of  $\text{Fe}^{2+}$ . The sharp bands are overtone and combination

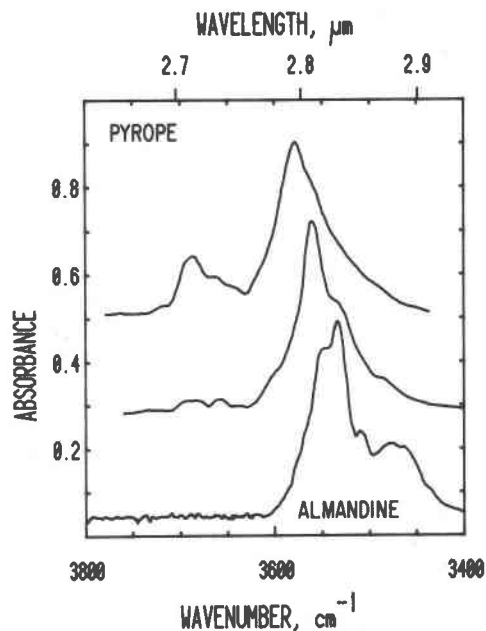


Fig. 6. Infrared spectra of typical members of the pyrope-almandine series showing the progression of spectral pattern with chemistry. From bottom to top: sample 23, plotted as 15 mm; sample 21, plotted as 20 mm; sample 49, plotted as 9.5 mm thick. Spectra recorded at  $-196^{\circ}\text{C}$ .

modes related to the fundamental O-H modes seen at  $\sim 3600\text{ cm}^{-1}$  (Fig. 5). None occur at  $\sim 5200\text{ cm}^{-1}$ , the diagnostic  $\text{H}_2\text{O}$  frequency. All the O-H is in the form of  $\text{OH}^-$  ions. The NIR region is difficult to study in detail because of very low intensities in the hydrous pyralspites, but no band at  $\sim 5200\text{ cm}^{-1}$  has been seen.

## Discussion

### Structure of the hydrous defect

The pyralspite garnets contain two classes of hydrous component: a structural component, and alteration-related water. The alteration-related hydrous component also includes hydrous inclusions and will not be discussed further. The structural hydrous component is of interest because: (1) the "water" contained in the garnet is a record of the environment of formation or later events, and (2) the garnet structure must be changed to accommodate a hydrous component and this may also change the physical properties of the garnet.

The criteria used to distinguish the structural hydrous component from alteration and inclusions, and the spectroscopic features that we have observed for the structural component, provide considerable information about its character. (1) The O-H defect responsible for the hydrous component is  $\text{OH}^-$ , not  $\text{H}_2\text{O}$ ; the diagnostic  $5200\text{ cm}^{-1}$   $\text{H}_2\text{O}$  band is not seen. (2) The IR spectra depend only on the chemistry of the garnet, not its origin. There is only one type of structural hydrous component. (3) Multiple

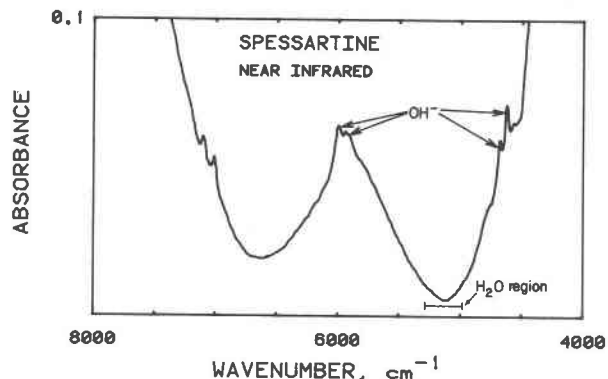


Fig. 7. Near-infrared spectrum of sample 78 showing the sharp overtone absorptions of O-H vibrations superimposed upon the extremely broad absorptions of trace  $\text{Fe}^{2+}$  in the sample, which occur at 7900, 5900 and 4200  $\text{cm}^{-1}$ . The overtone O-H absorptions occur at 7000, 6000, and 4600–4000  $\text{cm}^{-1}$ . No O-H absorption peaks occur in the 5200  $\text{cm}^{-1}$  region, indicating that there is no molecular water present.

$\text{OH}^-$  groups occur in close enough proximity to force them all to vibrate simultaneously, resulting in multiple peak patterns in which the relative intensities of the peaks are constant. These facts provide the basis for a structural interpretation of the hydrous component. It would be a mistake to automatically assume that the hydrogarnet substitution is present in natural pyralspites simply because they are hydrous. However, the above facts all fit an interpretation based on hydrogarnet.

In the hydrogarnet substitution, four  $\text{OH}^-$  groups replace  $\text{SiO}_4^{4-}$  tetrahedra (Cohen-Addad et al., 1967; Foreman, 1968). The four protons are slightly outside the volume of the tetrahedron as defined by the oxygen centers. These four O-H groups can be expected to yield a total of  $3N - 6 = 18$  vibrations, four of which are stretching vibrations and would occur near 3400 to 3700  $\text{cm}^{-1}$ . Not all four must occur, depending on the exact symmetry of the group. The presence of hydrogarnet substitution in an end-member garnet should be evidenced by an infrared spectrum in the 3500  $\text{cm}^{-1}$  region with up to four peaks. If complete garnet symmetry is maintained there will be two peaks.

The spessartine end-member pattern contains six peaks (Fig. 3) in violation of the four peak limit. However, the two lower-wavenumber peaks vary independently of the four high-wavenumber peaks (Fig. 5). They apparently arise from a separate defect. The grossular and almandine end-member patterns do not violate the four peak limit, and are consistent with the possibility of hydrogarnet substitution. Intermediate chemistry pyralspites are more complex, however. This complexity could be caused by multiple, non-hydrogarnet O-H defects. The simple behavior in binary systems suggests, however, that the multiple peaks are a reflection of site occupancy in the dodecahedral sites which contain the divalent ions. Figure 8 shows a portion of the garnet structure, a tetra-

dral site and its two dodecahedral neighbors. Not shown are four octahedral neighbors that share corners with the tetrahedral site. The presence of different cations sharing edges with a tetrahedral site "filled" by  $\text{H}_4\text{O}_4^-$  may be expected to significantly alter the spectra of the  $\text{H}_4\text{O}_4$  group by reducing the symmetry of the site and because of the large differences in cation size and cation oxygen bond lengths in the pyralspite garnets (Novak and Gibbs, 1971). The consistent change in the spectra in accord with the dodecahedral cation chemistries strongly suggests that the hydrous defect is located in the tetrahedral site.

Since the  $\text{H}_2\text{O}$  contents of the garnets studied are extremely low, considerably fewer than one  $\text{H}_4\text{O}_4$  substitution would occur per unit cell. Accordingly, there should be no coupling of vibrations between possible  $\text{H}_4\text{O}_4$  tetrahedra, and each may be considered independently. In a garnet of intermediate chemistry in a binary system, three combinations of dodecahedral neighbors (for instance, Mn-Mn, Mn-Fe, Fe-Fe) are possible and should yield three distinct infrared spectra. The intermediate-chemistry garnets' spectra can be described as composed of three components: one for each end-member, and a new component only seen in the intermediate chemistry samples. This new component appears to be due to mixed-neighbor pairs around tetrahedral sites. The spectral complexity in Figures 5 and 6 may be explained by this. The sites with neighboring Mg-Fe may give rise to absorption at  $\sim 3580 \text{ cm}^{-1}$  in pyrope-almandines, and the 3585  $\text{cm}^{-1}$  peak in spessartine-almandine may be assigned to sites with Mn-Fe neighbors.

The absence of resolvable fine structure in the intermediate garnets makes the assignment of actual O-H defect structures difficult. This apparent blurring of the fine structure arises as a result of intermediate chemistries, apparently due to the large number of local environments that are slightly different giving rise to a similarly large

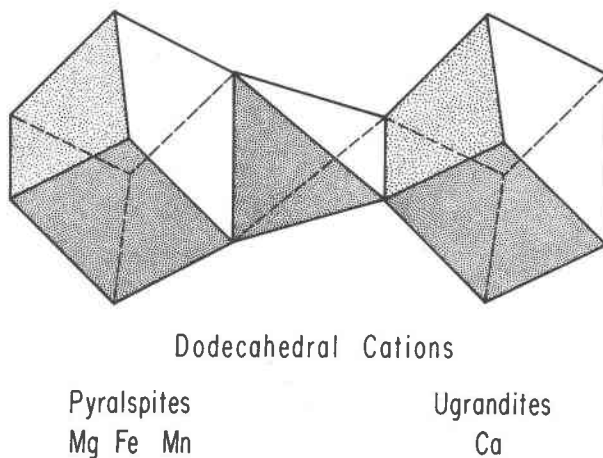


Fig. 8. Portion of the garnet structure showing the two dodecahedral sites that share edges with the tetrahedral site that may contain  $\text{H}_4\text{O}_4^-$ .



number of O–H defects that are slightly different and whose O–H absorption frequencies are offset by a few wavenumbers. The juxtaposition of many of these in an IR spectrum would result in a blurring of the sharp end-member pattern. This may be most clearly seen in the top three spectra of Figure 5.

The presence of three sets of peaks in intermediate-chemistry garnets is consistent with the hydrogarnet substitution, but is not compelling evidence. An example of one problem with this interpretation is seen in the spessartine spectra in Figures 3 and 5. The postulated Mn,Fe band at  $3585\text{ cm}^{-1}$  is seen in the supposedly end-member spectra. This sample is approximately  $\text{Mn}_{95}\text{Fe}_5$ , so some Mn–Fe pairs are expected, but the intensity of the  $3585\text{ cm}^{-1}$  peaks are far too large to be the result of random mixing of  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  dodecahedra with  $\text{H}_4\text{O}_4$  tetrahedra. If the postulated  $\text{H}_4\text{O}_4$  defects exist, they must heavily favor association with Mn–Fe neighbors. A similar effect is seen for Mg–Fe (Fig. 6) where the  $\text{Mg}^{2+}$  end-member pattern is never seen alone, and the postulated Mg–Fe pattern is dominant in all pyropes studied.

#### Occurrence and “water” content

The most hydrous pyralspite garnets encountered were spessartines and spessartine-almandines from igneous pegmatites. Garnets from metamorphic occurrences were much lower in structural  $\text{H}_2\text{O}$ , but frequently contained hydrous inclusions. Garnets of mantle origin were frequently hydrous, and is discussed in detail by Aines and Rossman (1984b). The majority of the garnets studied which were anhydrous were from the mantle, but only two samples of “crustal” origin were rigorously anhydrous. Sample 112 is from a region known for garnets occurring in metamorphosed mafic rocks, and sample 111 is from an alkali-olivine basalt flow. Both samples may have dehydrated as the host rock was cooling. Anhydrous crustal pyralspites are rare.

The garnets used in this study were chosen to represent the range of occurrences of pyralspites, but the range of water contents that we observed is quite limited, from 0.0 to 0.25 wt.% clustering around 0.1 to 0.15 wt.%. This suggests that the solubility of water in pyralspites is limited, and that the garnets we observed with greater than 0.2 wt.% may be saturated with water. The range that we observe, however, suggests that the water content of garnets may be a useful indicator of water fugacity pending experimental calibration of water solubilities.

#### Limitations to “water” concentrations in pyralspites

The hydrogarnet substitution has not been previously recognized as an important component of natural pyralspite garnets. The garnets studied here indicate that this lack of identification is due to the extremely low level of the substitution, and not to its frequency of occurrence. Two hypotheses have been previously advanced for the

apparent lack of hydrogarnet substitution in pyralspite, and may be applied instead to explain the consistently low levels. The first is that the  $\text{H}_4\text{O}_4^{4-} \rightleftharpoons \text{SiO}_4^{4-}$  substitution results in a large volume increase (Cohen-Addad, 1967; Meagher, 1980; Martin and Donnay, 1972) and as such is not favored at the high pressures typical of pyralspite formation. The second hypothesis (Zabinski, 1966) is that Mg–O and Fe–O bond lengths in pyralspites are slightly longer than the average lengths for these bonds in silicates, and that the additional increase in length that would occur during unit cell expansion associated with hydrogarnet substitution destabilizes the hydrous pyralspites. Ca–O bond lengths are comparatively short relative to such bond lengths in other silicates, favoring hydrogarnet formation in grossular–andradite garnets.

These theories may serve to explain the lack of pyralspites containing large amounts of water, such as the 2 to 6%  $\text{H}_2\text{O}$  hydrogrossulars described by Zabinski (1966). The relatively constant  $\text{H}_2\text{O}$  contents of the garnets in this study suggest that low solubility limits are indeed the controlling factor in  $\text{H}_4\text{O}_4$  substitution in pyralspites. Two studies of synthetic, hydrothermal pyralspites have been made in which the solubility was tested. Hsu (1980) synthesized grossular-spessartines at  $P_{\text{H}_2\text{O}} = 2\text{ kbar}$ ,  $T = 420\text{--}750^\circ\text{C}$ . The hydrogrossular Hsu generated gave IR spectra identical to those in this study, with peaks at  $3660$  and  $3620\text{ cm}^{-1}$ . The hydrosspessartines were identified on the basis of cell volume expansion (Hsu, 1968) analogous to the grossular-hydrogrossular expansion (e.g., Shoji, 1974; Ito and Frondell, 1967) and are reported to be metastable. However, the sharp bands reported by Hsu as related to  $\text{H}_4\text{O}_4$  in hydrosspessartine appear to be due to oil contamination (Ackermann et al., 1983), a conclusion with which we agree. Thus, there is no spectroscopic evidence of the hydrogarnet substitution given by these hydrothermally produced spessartines and their exact nature remains undetermined. This, combined with the metastability of the synthetic hydrosspessartines, makes it difficult to determine the expected extent of  $\text{H}_4\text{O}_4^{4-}$  substitution in natural spessartines.

Ackermann et al. (1983) studied hydrothermally produced pyropes. They found a single, sharp IR absorption band at  $3600\text{ cm}^{-1}$ , and a broad band centered near  $3470\text{ cm}^{-1}$  due to fluid inclusions. They report that the  $3600\text{ cm}^{-1}$  band is due to hydrogarnet substitution based on the peak location in synthetic hydrogrossular. Based on the evidence presented here, this seems unlikely because of the dependence of peak location on chemistry. While the pyrope end-member pattern is not well defined by this study, it occurs in the  $3670\text{ cm}^{-1}$  region based on the spectra of the Mg-rich garnets we studied. The presence of fluid inclusions leaves open the possibility of hydrous inclusions or alteration products in their pyropes. Fluid inclusion IR absorption dominates the spectra of their pyropes. Ackermann et al. report that the intensity of their  $3600\text{ cm}^{-1}$  band corresponds to a water content of

0.05% based on the muscovite peak-height molar absorptivity ( $\epsilon$ ) of  $170 \ell \text{ mole}^{-1} \text{H}_2\text{O cm}^{-1}$ . That value is based on peak height, not integral absorbance as reported here, but on the same basis the  $\epsilon$  from this study would be  $\sim 5 \ell \text{ mole}^{-1} \text{H}_2\text{O cm}^{-1}$  for intermediate chemistries, to  $\sim 150 \ell \text{ mole}^{-1} \text{H}_2\text{O cm}^{-1}$  for end members, measured using the most intense peak in the spectrum. Peak height molar absorptivities were not used in this study because of the ambiguity introduced by multiple peaks due to a single hydrous species.

Further work is required to determine the extent and nature of the hydrous component in synthetic pyropes, but the hydrous component seen by Ackermann et al. is present at similar concentrations to those in natural garnets. If they were in fact the same defects, this would be strong evidence of solubility being the limiting factor in natural hydrogarnet substitution. However, the infrared spectra observed by Ackermann et al. do not seem to be consistent with those we observed, and it is unlikely that both represent the same hydrous defect.

### Conclusions

Natural pyralspite garnets commonly contain a hydrous component at levels of 0.01 to 0.25 wt.%. Anhydrous pyralspites are rare. The hydrous component has the following characteristics:

1. The hydrogen speciation is  $\text{OH}^-$ , not  $\text{H}_2\text{O}$ .
2. Multiple hydroxides (2 to 4) vibrate together, indicating close proximity in the structure.
3. IR absorption spectra of different chemistry pyralspites are consistent with dodecahedral cation occupancy affecting a hydrogen defect in the tetrahedral site.

These characteristics are suggestive of the hydrogarnet substitution,  $\text{H}_4\text{O}_4^{4-} \rightleftharpoons \text{SiO}_4^{4-}$ , but other structural forms for the hydrogen defect(s) which have the above characteristics cannot be ruled out. Natural garnets also frequently contain a hydrous component in the form of alteration or included hydrous phases. The presence of a structural hydrous component may be best differentiated from these by infrared spectroscopy. The presence of hydrogarnet substitution in natural garnets may prove to be a useful indicator of water fugacity. However, the effects of alteration and hydrous inclusions must be carefully considered, particularly in metamorphic garnets where these effects are common.

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