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4 **IR Spectroscopy and OH⁻ in Silicate Garnet:**

5 **The Long Quest to Document the Hydrogarnet Substitution**

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Abstract

39 There has been much research undertaken on structural OH⁻ in various nominally anhydrous
40 minerals including the common silicate garnets (i.e., X₃Y₂Si₃O₁₂, where X = Mg, Fe²⁺, Mn²⁺ and
41 Ca and Y = Al, Fe³⁺ and Cr³⁺). However, it is still largely not understood where small
42 concentrations of H atoms are incorporated in the garnet crystal structure. In this work, the IR
43 single-crystal spectra of end-member or approaching end-member composition andradite, pyrope
44 and almandine are measured. Both a natural and synthetic andradite sample show a broad,
45 asymmetric OH-stretching mode at 3563 cm⁻¹ that splits into two narrower modes at lower
46 temperatures. They are located at 3575 cm⁻¹ and 3557 cm⁻¹ at 80 K with the higher wavenumber
47 mode being considerably more intense compared to that at lower energy. These results are
48 analyzed together with published IR spectra of synthetic end-member katoite, pyrope and
49 almandine also recorded at low temperature. These garnets show similar IR behavior with a broad
50 OH⁻ band at room temperature that splits into two narrower bands at lower temperatures and with
51 a similar intensity relationship as shown by andradite. This behavior is indicative of the
52 hydrogarnet substitution. The measured IR spectra of natural almandine- and pyrope-rich (Dora
53 Maira, Italy) crystals, on the other hand, show different spectroscopic features with several OH⁻
54 modes that are not consistent with the hydrogarnet mechanism. An analysis of the energy of the
55 OH⁻-stretching mode is made for various composition hydrogarnet clusters (i.e., X₃Y₂(O₄H₄)₃,
56 where X = Mg, Fe²⁺, Mn²⁺ and Ca and Y = Al and Fe³⁺) in terms of crystal-chemical properties
57 and local atomic configurations. The OH⁻ mode energy, which lies roughly between 3660 and
58 3550 cm⁻¹ at RT for various end-member garnets, is a function of the mass of the X- and Y-cations
59 due to mode coupling and/or mixing. In addition, the strength of the chemical bonding between
60 the X- and Y-cations and the O²⁻ anion of the OH⁻ dipole plays a role in affecting the wavenumber
61 of the OH⁻-stretching vibration. OH⁻ mode broadening observed in the spectra of end-member
62 garnets is primarily a result of thermal anharmonic disorder, especially with regard to the light H
63 cation. OH mode broadening in intermediate solid-solution composition garnets is a function of

64 both thermal effects and variations in local cation configurations around the OH⁻ dipole(s).
65 Published IR spectra of certain high-pressure pyrope-rich garnets, both synthetic and natural, are
66 analyzed and arguments made that OH⁻ can often be incorporated as the hydrogarnet or
67 hydropyrope substitution. IR spectra similar in appearance, having multiple relatively narrow OH
68 modes that are distinct from those indicating the hydrogarnet substitution, can be observed for
69 certain synthetic end-member and various composition natural pyropes from Dora Maira and some
70 natural spessartines. This indicates that other common OH substitution mechanisms, which have
71 yet to be determined, can also occur in different silicate garnet.
72 **Keywords:** hydrogarnet, silicate garnet, OH⁻ in minerals, IR spectroscopy, crystal chemistry.

73

INTRODUCTION

74 There has been much research undertaken on structural OH⁻ in nominally anhydrous minerals. A
75 number of different rock-forming silicates, for instance, have been shown to contain OH⁻ in
76 various, yet minor concentrations. There can be important geological consequences (Keppler and
77 Smyth, 2006). For example, there has been discussion on how many “oceans of water” could be
78 present in Earth’s mantle (Bell and Rossman, 1992) with its implications for global geochemical
79 and geophysical processes. One notable class of silicates that has received much study is the
80 common silicate garnets (X₃Al₂Si₃O₁₂ where X = Mg, Fe²⁺, Mn²⁺ and Ca and Y = Al, Fe³⁺ and
81 Cr³⁺) and they have been shown to have different OH⁻ concentrations arising from various
82 unknown substitution mechanisms. At low concentration, some researchers speak of OH⁻ defects.

83 It terms of studying structural OH⁻, IR single-crystal spectroscopy is generally the
84 analytical method of choice, because the OH⁻ dipole is strongly IR active. The IR spectra of a
85 large number of natural garnets have been recorded (e.g., Aines and Rossman, 1984; Rossman and
86 Aines, 1991; Bell and Rossman, 1992; Matsuyk et al., 1998). In spite of this, surprisingly, at least
87 to the non-expert, is the fact that it is not understood where or how small concentrations of H⁺
88 atoms are incorporated structurally in the various garnet species. This determination is not easily
89 made, because the OH⁻-stretching modes cannot be straightforwardly assigned. In addition, some
90 garnets, such as grossular-katoite compositions especially, show a great variability in the number
91 of their OH⁻ modes (Rossman and Aines, 1991). Of course, diffraction experiments could
92 theoretically give H positions in a crystal (e.g., Cohen-Addad et al., 1967; Lager et al., 1987), but
93 at low concentration levels this is not possible. Proton NMR study of synthetic hydrogrossular and
94 three natural grossulars showed in some cases the presence of four H-atom clusters (hydrogarnet)
95 and also two H-atom clusters (Cho and Rossman, 1993). Computations have not advanced to the
96 stage that IR or NMR spectra can be calculated well enough to interpret the experimental results
97 precisely. In terms of interpreting IR spectra and assigning OH⁻ modes, presently one is stuck with
98 empirical-based comparisons of spectra from different garnets and the possible conclusions that
99 derive from them.

100 The simple, standard starting point for interpreting IR spectra begins with the classic
101 hydrogarnet substitution (Aines and Rossman, 1984). That is, one substitutes locally an $\text{O}_4\text{H}_4^{4-}$
102 “group” (see Kolesov and Geiger, 2005, for a discussion of OH^- mode behavior in katoite) for a
103 SiO_4^{4-} one in the silicate garnet crystal structure. The idea derives from early work showing the
104 existence of “hydrogarnet”. Indeed, end-member katoite, $\text{Ca}_3\text{Al}_2\text{O}_{12}\text{H}_{12}$, can be synthesized in the
105 laboratory and it shows complete solid solution with grossular (Flint et al., 1941). This substitution
106 mechanism is, because so little is understood, the starting point or “fallback position” that is often
107 used when attempting to interpret the IR spectra of some silicates and especially silicate garnet
108 (Aines and Rossman, 1984) with low OH^- contents. It remains, however, just an unproven
109 assumption. It can be concluded, at the present time, that it is not understood precisely how minor
110 OH^- is structurally contained in garnet both synthetic and natural.

111 A major obstacle in understanding the nature of OH^- in garnet is that natural crystals are
112 normally solid-solution compositions and, moreover, they have also experienced relatively
113 complex geologic *P-T* histories. Thus, investigations have been made on synthetic crystals that
114 have simpler chemistries and which can be grown under well controlled *P(H₂O)-T* conditions
115 (e.g., Geiger et al., 1991; Armbruster and Geiger, 1993; Geiger et al., 1998; Withers et al., 1998;
116 Mookherjee and Karato, 2010; Geiger et al., in press). Indeed, the results show that synthetic
117 garnets often, but not always, show simpler IR spectra compared to those of naturals. Another
118 approach is to measure the spectra of nearly end-member natural garnets with the hope that they
119 will be simpler than crystals with more complex compositions. These two considerations are one
120 of the modus operandi for the present work. We present and analyze the IR single-crystal spectra
121 of natural nearly end-member andradite, pyrope and almandine garnets. The spectra are then
122 compared with their equivalent synthetic crystals that were grown at high pressure and high
123 temperature in the laboratory. OH^- mode behavior for the hydrogarnet substitution in the various
124 end-member garnets is interpreted for the first time by considering crystal-chemical properties and
125 the local atomic configurations around an OH^- dipole. This type of analysis is used further in an

126 attempt to assign different OH⁻ modes in spectra of various intermediate composition high-
127 pressure synthetic and natural pyrope-rich garnets.

128

129 **SAMPLES AND EXPERIMENTAL METHODS**

130 **Garnet samples**

131 The various garnet crystals, both synthetic and natural, measured via IR spectroscopy in this study
132 are described in Table 1. The precise outcrop locations for three of the pyrope crystals are given in
133 Simon and Chopin (2001) and their compositions in Geiger and Rossman (1994). The natural near
134 end-member andradite is from Val Malenco, Italy (collection of GRR) and the synthetic andradite
135 crystal is described in Armbruster and Geiger (1993) and Geiger et al. (in press). In terms of
136 almandine, three different natural samples, belonging to the some of the most almandine-rich
137 crystals found to date, were studied. The geologic occurrence and mineralogical characterization
138 of two of them are discussed in Woodland et al. (1995) and Aparicio et al. (2012). For IR
139 investigation, the crystals were slightly ground to two parallel sides to produce thin crystal
140 platelets and then finely polished.

141

142 **FTIR Single-Crystal Spectroscopy**

143 For the IR single-crystal measurements, the preparation and experimental conditions are similar to
144 those described in Aines and Rossman (1984) and Geiger et al. (1991). A few spectra were obtained
145 with a Thermo-Nicolet iS50 FTIR with a Continuum microscope accessory with a cryogenic MCT-
146 A detector and a CaF₂ beam splitter. Most spectra were collected, though, by attaching the doubly
147 polished crystal platelets over metal pinhole apertures of appropriate size (200 - 600 μm) and
148 measuring directly in the IR spectrometer sample compartment with an InSb detector. The sample
149 holder was carefully aligned to yield the strongest signal. Multiple spectra were collected on
150 different crystal regions that were clear and transparent under the binocular microscope and free
151 from any observable inclusions.

152 Low-temperature spectra were collected using a Continuum infrared microscope with a 15x
153 objective and a cryogenic HgCdTe detector. Samples were cooled with liquid nitrogen in a Linkam
154 FTIR 600 stage.

155

156 RESULTS

157 **Andradite**

158 The IR spectra of natural end-member andradite (GRR-134) from Val Malenco, Italy, from 296 K
159 down to 80 K are shown in Figure 1. The broad asymmetric OH⁻ band with a peak maximum at
160 3563 cm⁻¹ at room temperature (RT) splits into two OH⁻ bands that narrow and the more intense
161 band increases slightly in wavenumber with decreasing temperature. At 80 K, the two peak maxima
162 are located at 3575 cm⁻¹ and 3557 cm⁻¹. Very weak bands appear at higher wavenumbers in the
163 spectrum at 80 K. The RT spectrum of synthetic andradite (And #27) is the same as the natural
164 crystal in terms of the OH⁻ band placement (Fig. 1).

165

166 **Pyrope**

167 The IR spectra of four different composition pyrope-rich solid-solution crystals from different
168 geographic locations in the general area of Dora Maira, Italy, are shown in Figure 2. They are
169 shown with generally decreasing pyrope contents from bottom to top. There is a broadening of the
170 OH⁻ bands as one moves away from close to end-member pyrope into more intermediate
171 compositions. The spectrum of sample Masueria 2b with the most intense OH⁻ modes shows five
172 well-resolved OH⁻ bands located at 3660, 3651, 3641, 3618 (weak) and 3602 cm⁻¹ and a slight
173 shoulder on the high wavenumber side of the mode at 3660 cm⁻¹. The other pyropes show broadly
174 similar spectra.

175

176 **Almandine**

177 The spectra for the three different almandine samples (Table 1) are shown in Fig. 3. The IR
178 spectrum of the almandine (FR-3) from Collobrières, France, as described by Woodland et al.

179 (1995), is characterized by an OH⁻ band doublet showing possible minor structure. The two main
180 peaks have maxima at 3641 and 3623 cm⁻¹. There is also the possible presence of very weak OH⁻
181 bands (doublet) centered around ~3590 cm⁻¹. The spectrum of almandine from Zlaty Chlum near
182 Jeseník, Czech Republic, (JF-1) shows weak OH⁻ bands at 3562, 3523, 3501, and 3454 cm⁻¹.
183 Another almandine crystal from Collobrières, France, (A-5) shows very weak OH bands similar in
184 energy to those of the Zlaty Chlum sample.

185

186

DISCUSSION

187 IR Spectra of Compositionally End-Member or Nearly End-Member Garnets

188 **Synthetic and Natural Andradite.** The IR spectrum of end-member andradite (synthetic and
189 natural) shows a broad asymmetric mode OH⁻ at 3563 cm⁻¹ that splits into two narrower modes at
190 lower temperatures. We note that other natural andradite crystals can show spectra with more than
191 one OH⁻ band (Amthauer and Rossman, 1998; Adamo et al., 2009; Geiger et al., in press), but
192 many show this intense band at 3563 cm⁻¹.

193

194 **Natural Pyrope.** Garnet crystals from the Dora Maira, Italy, area are unique in terms of
195 composition (Chopin, 1984; Simon and Chopin, 2001), some being very close to end-member
196 pyrope - Mg₃Al₂Si₃O₁₂ (e.g., Masueria 2b/MAS2b and Ch-2 - Table 1). There is, though, a range
197 of compositional variability involving solid solution with almandine and grossular
198 ([Mg,Fe²⁺,Ca]₃Al₂Si₃O₁₂) giving, for example, crystals with about 76 mol % pyrope (i.e., sample
199 Masueria 2a/MAS 2a - Table 1). Pyrope-rich garnets from Earth's mantle have entirely different
200 petrologic origins and ranges of composition, containing considerably more grossular and
201 almandine, as well as sometimes knorringite, components (e.g., Bell and Rossman, 1992; Matsuyk
202 et al., 1998, as discussed below). The spectra of the four different crystals from Dora Maira are
203 similar to those presented in Rossman et al. (1989), who listed four OH⁻ bands at 3661.5, 3651.0,
204 3641.3, and 3602.1 cm⁻¹. The measurements herein confirm this, but we find, in addition, a weak
205 OH⁻ mode at 3618 cm⁻¹ as well as a slight shoulder on the high wavenumber side of the mode at

206 3660 cm^{-1} . There is a clear broadening of the OH^- bands with increasing almandine and grossular
207 content in the garnet (Fig. 2 - spectra bottom to top). The OH^- peak intensities are different among
208 the four samples indicating variable OH^- concentrations.

209
210 **Natural Almandine.** Three different natural almandine samples were examined and they
211 represent some of the most $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ -rich crystals that have been studied to date (cf., sample
212 JF-1, Table 1, was first studied by IR spectroscopy by Aparacio et al., 2012). The crystals of JF-1
213 and A-5 show similar IR spectra with OH modes at about 3562, 3523, 3501, and 3454 cm^{-1} (Fig.
214 3). The spectrum of almandine FR-3 is different and is characterized by two narrow higher energy
215 bands at 3641 and 3623 cm^{-1} . All three garnets show very different OH^- modes than the less
216 almandine-rich Wrangell sample in Aines and Rossman (1984), whose IR spectrum was proposed
217 to represent “typical” almandine. The intensity of the OH^- bands in all these almandines is weak.
218 The presented spectra show the most OH^- -rich parts of various crystals, as some other recorded
219 spectra show barely visible OH^- bands or none at all (i.e., there are variations in the OH^- contents).
220 Low OH^- contents appear to be a general characteristic of many natural almandine crystals (also
221 unpublished results of C.A.G and G.R.R.).

222
223 **An Analysis of OH-Mode Behavior in the IR Spectra of Garnet**
224 **The Hydrogarnet Substitution in End-Member Garnets.** Over the years, the IR spectra of a
225 large number of garnets, both natural and synthetic, have been measured. In many cases, the
226 observed OH^- stretching bands, which may be one or more in number and showing a range of
227 wavenumbers, have been suggested to represent the hydrogarnet substitution (e.g., Aines and
228 Rossman, 1984; Geiger et al., 1991; Withers et al., 1998). However, the underlying scientific
229 arguments for these proposals are effectively non-existent for anything other than hydrogrossular
230 (katoite), itself. We think, though, that progress in this question can be made using the IR results
231 from this work, together with spectra of other garnets given in the literature, by analyzing the
232 nature of the OH^- bands in terms of the structural and crystal-chemical properties of garnet.

233 To start the analysis, we consider the IR spectrum of synthetic katoite, $\text{Ca}_3\text{Al}_2\text{O}_{12}\text{H}_{12}$, a
234 non-silicate garnet, which has been studied at temperatures from 293 K (RT) down to 10 K
235 (Kolesov and Geiger, 2005). Its OH^- -mode behavior is well documented and understood at least
236 between 293 K and 80 K. The spectrum of katoite shows a single intense and broad asymmetric
237 OH^- -stretching mode at 3662 cm^{-1} at RT, which narrows and shifts to higher energies with
238 decreasing temperature. With further decreasing temperature and first at about 80 K, a second
239 much less intense OH stretching mode at about 3600 cm^{-1} appears. This two OH-band pattern
240 characterizes the IR spectrum of katoite with the notable addition of weaker fine structure
241 appearing on these two strongest modes below about 80 K. The nature of these fine structure OH
242 modes is not understood.

243 The IR spectrum of both natural end-member (Val Malenco) and synthetic andradite are
244 the same in terms of the energy of the single asymmetric OH^- mode occurring at 3563 cm^{-1} . This
245 agreement is notable and has not been observed before for other natural and synthetic end-member
246 garnet species to the best of our knowledge. With decreasing temperature, this OH band begins to
247 narrow and it splits into a more intense higher energy mode and a less intense mode at low
248 wavenumbers (Fig. 1 & Fig. 4). We think this behavior reflects the hydrogarnet substitution in
249 andradite for two reasons. First, it is similar to that observed for katoite upon cooling. Second,
250 both natural end-member and synthetic andradite show the same IR spectrum. Thus, it can largely
251 be ruled out that OH defects, related to the presence of other garnet chemical components,
252 especially those containing highly charged elements (e.g., Ti^{4+} - see below), are not found in
253 significant amounts in both garnets. *P* and *T* conditions of formation between the two samples are
254 also widely different. The synthetic was grown at $1200\text{ }^\circ\text{C}$ (Geiger and Armbruster, 1997),
255 whereas the natural crystal comes from a much lower temperature serpentinite.

256 This interpretation for the IR hydrogarnet signature is further supported by the spectra of
257 most synthetic hydrothermally-grown pyropes recorded at RT and 80 K (Geiger al., 1991, see,
258 however, discussion below on other synthetic pyrope crystals). Once again, a relatively broad
259 asymmetric OH^- mode at 3629 cm^{-1} , at RT splits upon cooling into two narrow bands at 80 K

260 (3638 and 3614 cm^{-1} - Fig. 4) and they show a similar intensity relationship as the OH^- -mode
261 doublet in katoite and andradite. Synthetic almandine shows a more complex IR spectrum with
262 two broad OH bands at RT (Fig. 4), but the most intense OH^- band at 3613 cm^{-1} , which we assign
263 to the hydrogarnet substitution, behaves in a similar manner (Geiger et al., in press) as the three
264 garnets discussed above. At 80 K, three narrow OH^- bands derive from the RT band at 3613 cm^{-1} .
265 However, the typical “hydrogarnet” doublet occurs once again and is the most prominent of the
266 three bands. Finally, the assignment of the respective OH^- modes to a hydrogarnet substitution in
267 the various end-member garnet species is consistent with their wavenumber behavior as based on
268 their structural and crystal-chemical properties, as discussed next.

269 The cubic silicate garnet structure, space group $Ia-3d$, is characterized by three cation sites
270 (X, Y, and Si) located on special crystallographic sites and a single oxygen anion located at a
271 general position (i.e., it has positional freedom in x , y and z). Katoite has the same space group
272 and, here, the Si cation is absent and is charged balanced by the presence locally of four H^+ cations
273 (i.e., the so-called hydrogarnet substitution). Figure 5 shows the local atomic environment around
274 a single OH^- group that serves as one dipole of the hydrogarnet O_4H_4 cluster without a neighboring
275 Si cation. The oxygen anion is bonded to one Y cation, two X cations and the H atom. The bond
276 with H gives the stretching vibration of the OH^- dipole that is so strongly IR active. It has been
277 argued or implied in various works that the energy of this OH stretching mode depends on the
278 $\text{OH}\cdots\text{O}$ length in the garnet, that is, the strength of the hydrogen bonding. The relationship
279 between $\text{OH}\cdots\text{O}$ bond length and the vibrational stretching energy of the OH^- bond for many
280 different compounds is well known (e.g., Nakamoto et al., 1955; Libowitzky, 1999). The analyses
281 show that the OH^- stretching energy is not a meaningful function of the $\text{H}\cdots\text{O}$ length, when it is
282 greater than about 2.0 Å. In other words, OH^- vibrational energies between roughly 3500 and 3700
283 cm^{-1} do not give any unique information on the $\text{H}\cdots\text{O}$ bond length. Indeed, a free OH^- dipole is
284 considered to vibrate at approximately 3560 cm^{-1} (Libowitzky, 1999). Thus, it makes no sense to
285 argue that the varying OH^- -mode wavenumbers observed for the different end-member garnets are
286 related to differences in H-bonding lengths (i.e., H bonding is stronger in OH^- -bearing andradite

287 than in OH⁻-bearing pyrope, for example). The lack of measurable hydrogen bonding in garnet is
288 shown, moreover, by the IR spectra made as a function of temperature. For katoite, andradite,
289 pyrope, and almandine, the most intense OH⁻ mode increases in energy with decreasing
290 temperature, whereas the general observation for H-bonded systems should be just the opposite,
291 namely H-bonding increases in strength with decreasing temperature.

292 We think, instead, that the OH⁻-bearing vibrational energy in the different end-member
293 garnets is largely a function of two crystal-chemical properties. The first is atomic mass. Because
294 the O²⁻ anion in hydrogarnet is bonded to three cations and the H atom (Fig. 5), whereby the
295 former cations are considerably heavier, the energy of the OH⁻ stretching vibration will be affected
296 via mode coupling through the O²⁻ anion. That is, the heavier the combined mass of the X- and Y-
297 cations, the lower the energy of the OH⁻ mode. The second important crystal-chemical effect
298 involves the strength of the X(1)-O, X(2)-O and Y-O bonds. The stronger they are, the weaker the
299 OH⁻ bond will be. This general effect is, for example, well documented in crystal hydrates
300 containing an alkali or alkaline-earth cation that is bonded to the oxygen anion of an H₂O
301 molecule (Lutz, 1988). The observation is, the stronger the cation-oxygen interaction, the weaker
302 the intramolecular OH bond (i.e., lower energy) of the H₂O molecule. In terms of chemical
303 bonding in silicate garnets it has been shown, using calculated bond valences, that Ca-O bonding
304 in andradite is stronger than Fe²⁺-O bonding in almandine and Mg-O bonding in pyrope
305 (Armbruster and Geiger, 1993). Thus, the OH bond in andradite will be weakened compared to
306 that of the latter two garnets.

307 Consider the bond effect in garnet further. Rossman and Aines (1992) argued that end-
308 member katoite and OH⁻-poor grossular components in a Ca₃Al₂(SiO₄)_{1-x}(O₄H₄)_x solid-solution
309 crystal are characterized by two OH⁻ stretching modes at 3660 and 3598 cm⁻¹ at RT, respectively.
310 At first glance, this might appear to be at odds with the analysis given above, because the local
311 atomic configuration for a hydrogrossular and katoite cluster might be considered the same (Fig.
312 5). However, only the masses of atoms in the clusters are the same but not the Ca-O bond lengths.
313 In silicate grossular the Ca-O bond lengths are Ca(1)-O(4) = 2.322(1) Å and Ca(2)-O(4) =

314 2.487(1) Å (Geiger and Armbruster, 1997) and in end-member katoite $\text{Ca}(1)\text{-O}(4) = 2.465(2)$ Å
315 and $\text{Ca}(2)\text{-O}(4) = 2.511(1)$ Å (Lager et al., 1987). Ca-O bonding is stronger in grossular than in
316 katoite (this analysis ignores, of course, the fact that the Ca-O bonds in a local hydrogrossular
317 cluster should be a bit longer than the Ca-O bonds in the much more prevalent silicate grossular
318 “matrix”. That is, there is local bond relaxation in the solid solution). Summarizing, OH bonding
319 will be weaker for hydrogrossular-like clusters than for katoite clusters in a $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{1-x}(\text{O}_4\text{H}_4)_x$
320 solid-solution crystal.

321 The above analysis does not consider thermal effects, which are clearly reflected in the
322 temperature-dependent IR measurements. Indeed, diffraction measurements made on katoite
323 (Lager et al., 1987; Lager et al., 2002) at RT show that the H/D atoms are characterized by large
324 amplitudes of vibration and we think this dynamic behavior causes the OH^- mode broadening.
325 Atomic amplitudes of vibration, especially for the light H atom, are damped at lower temperatures,
326 resulting in substantial OH^- mode narrowing and then splitting. Kolesov and Geiger (2005)
327 analyzed the nature of OH^- mode widths for both IR and Raman spectra in the case of katoite. It
328 can be argued that the natural (non thermal) half widths for OH modes are less than 20 cm^{-1} at
329 temperatures below 10 K.

330 In conclusion, an analysis of the wavenumber behavior for the single OH^- stretching mode
331 at RT, arising from the presence of hydrogarnet ($\text{O}_4\text{H}_4^{4-}$) groups in various garnets, shows that it
332 should decrease, as observed, in the order katoite (3662 cm^{-1}), pyrope (3629 cm^{-1}), almandine
333 (3613 cm^{-1}), grossular (3598 cm^{-1}), and andradite (3563 cm^{-1}).

334 335 **OH-Mode Widths and Energies in End-Member and Intermediate Composition Garnets.**

336 The half-widths of the OH^- stretching band are greater for intermediate composition natural
337 garnets with two or more different X-cations compared to those of end-member or nearly end-
338 member compositions having just one predominant X-cation (e.g., Aines and Rossman, 1984).
339 The modes are broader because of the presence of different local-cation distributions. That is,
340 static related local-atomic and -structural heterogeneity contributes to mode broadening in addition

341 to atomic thermal effects. This can be illustrated by considering the possible nature of cation
342 mixing at the X-site, as in a hypothetical $[\text{Mg}, \text{Fe}^{2+}, \text{Ca}]_3\text{Al}_2\text{Si}_3\text{O}_{12}$ aluminosilicate garnet (Fig. 6).
343 This figure shows an edge-shared dodecahedral(D)-tetrahedral(T) chain (Fig. 6a) with a
344 hypothetical distribution of three different X-cations and a local T-D cluster (Fig. 6b) in the garnet
345 structure, respectively. Every SiO_4 or O_4H_4 group in garnet has two edge-shared and four corner-
346 shared dodecahedra (a single OH dipole of an O_4H_4 group is illustrated in Fig. 5). In the case of an
347 end-member garnet, the local X-cation environment around every $\text{O}_4\text{H}_4^{4-}$ group/OH⁻ dipole is the
348 same (i.e. there is no local compositional and structural heterogeneity). However, in the case of
349 intermediate composition garnets there should be a range of $\text{O}_4\text{H}_4^{4-}$ groups or OH dipoles
350 associated with different local X-cation configurations. Each local-atomic configuration will be
351 characterized by its own “static” structural properties, for example, bond lengths and angles that
352 vary with the sizes of the cations involved (see general discussion in Bosenick et al., 2000, and
353 Freeman et al., 2006).

354 In addition, the masses of the X-cations in the various configurations will be different.
355 These local variations in structural properties and masses will give rise to a distribution of OH⁻
356 stretching band mode energies (the situation is, for example, not totally dissimilar to that in the
357 amphiboles, which are much better understood in terms of their OH⁻ mode behavior, see e.g.,
358 Hawthorne and Della Ventura, 2007. Here, separate OH⁻ modes can even be used to describe the
359 distribution of different cations in neighboring M sites). In other words, in terms of Fig. 6a and
360 with a typical pyrope-rich mantle garnet, for example, there will be statistically a large fraction of
361 local D(Mg)-T-D(Mg) configurations, but also D(Mg)-T-D(Fe^{2+}), D(Mg)-T-D(Ca), D(Ca)-T-
362 D(Fe^{2+}), D(Ca)-T-D(Ca), and D(Fe^{2+})-T-D(Fe^{2+}) ones. Their relative percentage will depend on
363 the bulk composition of the crystal and also, importantly, on any energetically preferred
364 configurations (i.e., possible short-range cation ordering - see Palke et al., 2015). The latter effect
365 is complex in nature and not understood for garnet. Indeed, there could well be certain preferred
366 local atomic configurations (O_4H_4 or SiO_4 groups surrounded by a non-random distribution of X-
367 cations) in intermediate composition garnets. Of the various silicate garnet species, it is only

368 grossular (and possibly andradite) that shows complete solid solution with a hydrogarnet end
369 member (Flint et al., 1941). Pyrope and almandine, in comparison, show much less tendency
370 toward a hydrogarnet solid solution. The simple crystal-chemical interpretation for this is that
371 garnets with the larger Ca cation, and a concomitant larger unit-cell volume (e.g., grossular -
372 12.529 J/bar vs. pyrope - 11.316 J/bar and almandine - 11.523 J/bar), offer a more “expanded
373 crystal structure” that allows for considerable incorporation of the larger O₄H₄ groups.

374 In conclusion, this crystal-chemical-based analysis offers a framework to begin to interpret
375 OH⁻ mode energies and widths related to various hydrogarnet components in both end-member
376 and intermediate composition garnets. Former works that simply considered a specific OH⁻ mode
377 energy or energies among different garnet species and their compositions in order to identify, say a
378 common hydrogarnet substitution, are based on wrong premises. Such a simple analysis cannot be
379 correct. A first attempt to assign OH⁻ IR modes for the hydrogarnet substitution in intermediate
380 garnets, as well as understanding the physical nature of their energies, will now be made.

381 382 **The Hydrogarnet and Other OH⁻ Substitutional Mechanisms in High-Pressure Garnets.**

383 Considerable effort has focused on investigating OH⁻ in synthetic (Geiger et al., 1991; Withers et
384 al., 1998; Mookerjee and Karato 2010; Thomas et al., 2015) and natural (Bell and Rossman, 1992;
385 Matsuyk et al., 1998) high-pressure garnets, because the question of the bulk water content in
386 Earth’s interior is of great geochemical and geophysical interest. We analyze various published IR
387 spectra in light of the results on end-member garnets and the crystal-chemical analysis given
388 above.

389 To start, Figure 7 shows the IR spectra for a synthetic end-member pyrope (P-13 - Geiger
390 et al., 1991) and a high *P-T* (18 GPa and 1800 °C) synthetic solid-solution garnet of composition
391 (Mg_{2.50}Fe²⁺_{0.59})(Si_{0.06}Al_{1.76}Cr_{0.08}Fe³⁺_{0.02})[SiO₄] described in Thomas et al. (2015). Both garnets
392 show the characteristic broad asymmetric OH⁻ mode with a maximum at about 3630 cm⁻¹. We
393 conclude that the latter OH⁻-bearing garnet has a hydropyrope-like substitution (i.e., O₄H₄ groups
394 surrounded by Mg cations - Fig. 6). This proposal could be tested by measuring this crystal’s IR

395 spectrum at low temperatures to see if the characteristic “OH⁻-doublet” appears. The IR spectra of
396 other majorite-containing garnets in Thomas et al. (2015) show different spectra which, in some
397 cases, may reflect variations in composition and, thus, local cation configurations.

398 The IR spectra of natural pyrope garnets are different in appearance. Many various
399 composition pyrope-rich garnets, deriving from different mantle-rock types, were studied
400 spectroscopically in detail by Bell and Rossman (1992) and Matsuyk et al. (1998). There is, in
401 general, good agreement in the observations from both investigations, which are more
402 mineralogical-petrological in nature and where assignments of the OH⁻ modes were not made. OH⁻
403 -mode behavior is analyzed, here, using structural and crystal-chemical properties as introduced
404 above.

405 Presently, it is not understood why natural pyropes show spectra with two or three or more
406 OH⁻ modes and with wavenumbers different than that of the single OH⁻ mode at 3629 cm⁻¹
407 observed for most synthetic pyropes. Bell and Rossman divide their studied garnets, based on their
408 characteristic IR spectra and OH⁻ mode energies and intensities, into three groups, namely “high-,
409 middle- and low-wavenumber” types. Matsuyk et al. propose a similar classification with three
410 main spectral groups labeled as I, II and III, as characterized by their OH⁻-mode wavenumbers of
411 3645-3662 cm⁻¹, 3561-3583 cm⁻¹ and 3515-3527 cm⁻¹, respectively. The IR spectra of three
412 different pyropes from mantle xenoliths (LAC-40, Lace, S. Africa and RTF-2 and RTF-4
413 Rietfontein – Bell and Rossman, 1992) are shown in Fig. 8. We start our analysis with garnet
414 RTF-2 that shows an asymmetric OH⁻ mode with a maximum at about 3650 cm⁻¹. It could
415 potentially, based on the arguments made above, represent a hydrogarnet substitution. However,
416 its wavenumber is greater than any OH⁻ mode measured in any end-member silicate garnet.
417 Therefore, at first glance, it could be concluded that it does not represent a hydrogarnet
418 substitution. However, there is explanation for its high wavenumber and it follows from an
419 analysis of X-O bond lengths in binary X₃Al₂Si₃O₁₂ garnet solid solutions (Bosenick et al., 2000;
420 Freeman et al., 2006; Geiger, 2008). We propose that this OH⁻ mode at roughly 3650 cm⁻¹
421 represents a hydropyrope-like cluster in a solid-solution silicate garnet crystal. The OH⁻ mode is

422 greater by about 20 cm^{-1} wavenumbers than that for the OH^- mode in end-member pyrope (3629
423 cm^{-1}), because the associated Mg-O bonds in the hydropyrope cluster will be slightly greater in
424 length compared to those in end-member silicate pyrope (note also that the wavenumber
425 difference between the OH^- mode for katoite and OH^- -poor grossular (locally hydrogrossular
426 clusters) is about 60 cm^{-1}). That is, the presence of significant amounts of Ca in the garnet solid
427 solution act to expand the average unit-cell volume compared to that in end-member pyrope and
428 the Mg-O bonds will be slightly lengthened accordingly. It follows, then, that the OH^- stretching
429 mode in a local hydropyrope cluster in a solid-solution crystal will be stronger and, thus, will
430 vibrate at a higher energy compared to that of a local hydropyrope in nearly end-member pyrope.

431 Most mantle pyrope-rich garnets, though, are marked by the most intense OH^- mode
432 located at approximately 3570 cm^{-1} (middle-wavenumber type of Bell and Rossman or group II of
433 Matsuyk et al. - Fig. 8 samples RTF-4 and LAC 40 - and also see spectra “a” and “p” in Fig. 2 of
434 Bell and Rossman, 1992). We assign this mode to a hydrogrossular-like-cluster contained in a
435 pyrope-rich solid-solution crystal. The Ca-O bonds in the hydrogrossular cluster will be slightly
436 shorter compared to those clusters in nearly end-member grossular and, thus, stronger. Therefore,
437 the OH^- bond will be weaker and its stretching energy will lie at lower wavenumbers compared to
438 OH^- in nearly end-member grossular (i.e., 3598 cm^{-1}). The mass effect seems to play a secondary
439 role in affecting the energy of this OH^- mode in the pyrope-rich solid solutions. Bell and Rossman
440 (1992 - p. 169) write “Preliminary indications are that the position of this band maximum shifts in
441 a regular fashion to lower wavenumber as a function of decreasing $\text{Mg}/(\text{Mg} + \text{Fe})$ ratio in
442 megacrysts.” We interpret this as indicating that the local hydrogrossular-like-clusters are
443 becoming statistically slightly more Fe^{2+} rich (Fig. 6b). Finally, it is important to note that this
444 band at 3570 cm^{-1} is often the most intense OH^- mode observed in the spectra of mantle pyropes
445 (Bell and Rossman, 1998). We think this is reflecting the fact that a hydrogrossular cluster is
446 energetically more favorable than say a hydropyrope cluster in a solid-solution garnet for the
447 crystal-chemical reasons discussed above.

448 To end the analysis, we address the third major OH^- mode type that can be observed in mantle

449 pyropes. It is located at roughly 3512 cm^{-1} (Bell and Rossman, 1992) or between $3515\text{-}3527\text{ cm}^{-1}$
450 (Matsuyk et al., 1998). The latter workers argue that this mode is associated with relatively TiO_2 -
451 rich garnets (about $> 0.4\text{ wt. \%}$). This proposal is consistent with the IR spectra of synthetic Ti-
452 bearing pyropes that have multi-OH-band spectra that show a low-energy mode at 3526 cm^{-1} (Fig.
453 8 –Geiger et al., 2000). It is also notable that these synthetic Ti-bearing pyropes show a broad OH
454 mode at about 3630 cm^{-1} at RT (Fig. 8), which splits into two narrow bands at 78 K (Geiger et al.,
455 2000).

456

457 **Other Non-Hydrogarnet OH⁻ Substitutional Mechanisms in End-Member Garnet**

458 The results and analysis given above are a strong argument that the hydrogarnet substitution can
459 occur in several end-member or nearly end-member silicate garnets and that it is characterized by
460 a single, broad OH⁻ mode at RT. However, some nearly end-member natural garnets can also show
461 more complex multi-OH⁻-band spectra, where the bands are relatively narrow and have energies
462 unlike those garnets containing a hydrogarnet component (almandine - this work; pyrope - this
463 work and Rossman et al., 1989; grossular - Rossman and Aines, 1991; spessartine - Aines and
464 Rossman, 1984). The immediate conclusion is that there must be other structural or defect
465 mechanisms for incorporating OH⁻ in garnet. Figure 9 shows the IR spectrum of a nearly end-
466 member pyrope (i.e., Masueria 2b - Table 1), a synthetic pyrope grown from a gel-starting
467 material (Geiger et al., 1991), and a natural nearly end-member spessartine (Rutherford Mine,
468 Amelia Courthouse, Amelia Co., VA). All three garnets show similar IR patterns with the same
469 number of five OH⁻ bands and having a similar wavenumber distribution (The OH⁻ modes in
470 spessartine lie at lower energies because, again, Mn^{2+} is heavier than Mg^{2+}). The only difference is
471 in the relative intensities among some of the bands. These three garnets apparently have OH⁻
472 located at common structural sites and they are different than that of the “standard” hydrogarnet
473 substitution. The narrow half widths of the OH⁻ bands further characterize the spectra of these
474 garnets and it can be argued that the vibrational freedom of the OH groups is more restricted
475 compared to that for OH⁻ groups in the hydrogarnet substitution.

476

477

IMPLICATIONS

478 This work outlines how the hydrogarnet substitution can be identified in the IR spectra of nominally
479 anhydrous end-member as well as some intermediate composition garnets. Low-temperature
480 vibrational spectroscopic measurements are important in this determination. Spectra recorded at
481 low-temperature are also necessary to fully understand the vibrational behavior (energetic and
482 bonding) of H₂O molecules occurring in various microporous silicates (e.g., Kolesov and Geiger,
483 2002; 2005). It appears to be a common phenomenon that the large amplitudes of vibration
484 associated with the light H atom in many OH⁻ groups and H₂O molecules in ionic crystals at RT
485 causes a broadening of their respective vibrational modes. At low temperatures the vibrations are
486 damped and these modes narrow and often split revealing more spectral and, thus, structural
487 information.

488 A long and continuing goal in the investigation of H₂O at low concentrations in nominally
489 anhydrous silicates, and here garnet, is to assign different vibrational OH⁻ stretching modes to
490 various substitutional mechanisms and structural sites. The spectroscopic and crystal-chemical
491 analysis undertaken in this work is a step in this direction. The results show that for silicates with
492 relatively complex structures more effort must be made to understand local crystal-chemical
493 properties and atomic configurations in the immediate vicinity of any OH⁻ groups. This is necessary
494 to interpret both the possible number of OH⁻ modes as well as their energies. It follows, conversely,
495 that it may be possible in some cases to use OH⁻ stretching modes in nominally anhydrous minerals
496 as a probe to investigate the nature of short-range-atomic order in intermediate solid-solution
497 compositions (cf., to the case of OH-bearing minerals - Hawthorne and Della Ventura, 2007).

498 The role of atoms occurring in minor concentrations in garnet, especially those that lead to
499 deviations in the nonstoichiometry of the formula unit from 3:2:3:12 (e.g., Na, B, Li, Zr, P, F), as
500 well as possible point defects, and their possible effect on OH incorporation, needs further study.
501 Work on compositionally simpler, well-characterized synthetic crystals will be essential in this

502 regard. Also important to consider is the role of trivalent cation substitutions at the tetrahedral site,
503 where H^+ may act as the charge-compensation ion associated with a single OH^- group.

504 Finally, the results and proposals, herein, could be of significance in terms of efforts to
505 quantify the small concentrations of OH^- in garnet solid solutions. It can be expected that molar
506 absorption coefficients for OH^- could be a function of the local structural type of OH^- . Existing
507 calibrations with a single absorption coefficient, based on several OH^- modes deriving from
508 different OH^- sites or groups (e.g., hydroxyrope, hydrogrossular, hydrospessartine), may not be
509 quantitative. It could be expected that each OH^- substitution mechanism (i.e., with different dipole
510 interactions) will have its own characteristic molar absorption coefficient. The appears to be the
511 case with olivine (Kovács et al., 2010). Concentrating calibration work just on the mode (or modes)
512 related to a hydrogarnet substitution (or different local hydrogarnet substitutions in solid-solution
513 crystals), as outlined herein, could permit a better understanding of OH^- concentration as a function
514 of *P-T-X* crystallization conditions. Of course, any analytical method giving bulk OH^- contents
515 could be difficult to interpret.

516

517

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644 Table 1. Description of natural and synthetic garnet samples measured in this study.

Sample Label	Locality (Source)/ Synthesis Conditions/ Composition	Sample Description & Composition	Mole % ($\pm 1-2$) End Member
Pyrope MAS-2a	Masueria, Italy (Ch. Chopin; Simon & Chopin, 2001; Geiger & Rossman, 1994)	Pinkish to light red transparent single crystal containing various inclusions.	Py(76)
Pyrope MAS-2b	Masueria, Italy (Ch. Chopin; Simon & Chopin, 2001, Geiger & Rossman, 1994)	Very light pinkish transparent single crystal.	Py(99)
Pyrope SB	San Bernardo, Italy (Ch. Chopin; Simon & Chopin, 2001; Geiger & Rossman, 1994)	Light pinkish transparent single crystal.	Py(82)
Pyrope Ch-2	“Dora Maira”, Italy (Ch. Chopin, exact locality unknown; Geiger & Rossman, 1994)	Colorless transparent single crystal.	Py(98)
Andradite #27	$T = 1200\text{ }^{\circ}\text{C}$ & $P = 20\text{ kbar}$, w/ PtO_2 (Armbruster & Geiger, 1993; Geiger et al., submitted)	Loose synthetic polycrystalline product (An_{100}) with some individual crystals up to roughly $300\text{ }\mu\text{m}$ in size. Yellow greenish to golden in color. Isotropic.	An(100)

Andradite GRR-134	Val Malenco, Italy (Amthauer & Rossman, 1998)	Light green transparent single crystal. Anisotropic.	An(99)
Almandine A-5	Collobrières, France (C. Ferraris, Paris, Muséum national d'histoire naturelle, Geiger & Rossman, 1994)	Single crystals mm size. Compositionally homogeneous and unzoned. Inclusions.	Al(94)
Almandine FR-3	Collobrières, France (Woodland et al., 1995)	Crystals up to cm size. Metamorphosed ironstone. Compositionally homogeneous and unzoned. Numerous cracks and some inclusions.	Al(93)
Almandine JF-1	Zlaty Chlum near Jeseník, Czech Republic (Aparicio et al., 2012)	Metasedimentary rocks.	Al(95)

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Figures

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651 Figure 1. IR single-crystal spectra of natural end-member andradite from Val Malenco, Italy,
652 (Table 1) at 296 K, 198 K, 123 K, 89 K and 80 K (from bottom to top). The broad asymmetric OH
653 band at room temperature has a peak maximum at 3563 cm^{-1} and two major peaks at 3575 cm^{-1}
654 and 3557 cm^{-1} at 80 K. The RT spectrum of synthetic andradite #27 (black) is shown at the bottom
655 (Geiger et al., in press) also with a single band at 3563 cm^{-1} at RT.

656

657 Figure 2. IR single-crystal spectra of various composition pyrope-rich crystals from Dora Maira,
658 Italy (Table 1). They are shown with increasing almandine and slight grossular contents (decreasing
659 pyrope component) from bottom to top. For the most “water-rich” crystal (Masueria 2b) the five
660 main OH band energies are at 3660 , 3651 , 3641 , 3618 (weak) and 3602 cm^{-1} and a weak shoulder
661 on the high-energy wing of the band at 3660 cm^{-1} . The OH modes broaden with decreasing pyrope
662 content in more intermediate compositions due to variations in local atomic configurations (see
663 text).

664

665 Figure 3. IR single-crystal spectra of the three almandine-rich crystals (Table 1). The sample FR-3
666 is 0.30 mm, sample A-5 0.22 mm, and sample JF-1 0.36 mm thick. The sloping background is due
667 to the low-energy flank of an intense electronic transition related to Fe^{2+} that is centered at about
668 4400 cm^{-1} (Geiger and Rossman, 1994). The OH band energies are given in the text.

669

670 Figure 4. Comparison of IR spectra of end-member synthetic pyrope (sample P-13, 0.273 mm
671 thick, from Geiger et al., 1991), almandine (A-2, ~ 0.90 mm thick, in Geiger et al., in press) and
672 natural andradite (GRR-134, 1.185 mm thick, this work) at room temperature and $\sim 80\text{ K}$ (liquid
673 N_2). For synthetic pyrope the OH band at 3629 cm^{-1} at RT splits into two narrow OH bands at
674 3638 and 3614 cm^{-1} . For synthetic almandine the most intense broad OH band at 3613 cm^{-1} at RT

675 splits into three narrow OH bands at 3663 (weakest), 3617 (intense) and 3590 (weak) cm^{-1} at about
676 80 K with the latter two assumed to represent the hydrogarnet substitution.

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678 Figure 5. Local atomic environment around a single OH dipole in the case of katoite (no Si
679 cation). The oxygen anion (red) in the garnet structure is bonded to one Y(Al) cation (blue), two
680 X(Ca) cations (yellow - in hydrogrossular with bond lengths of $\text{Ca1-O(1)} = 2.462(3) \text{ \AA}$ and Ca(2)-
681 $\text{O(4)} = 2.520(3) \text{ \AA}$ (Lager et al., 2002) and a H atom (pink).

682

683 Figure 6. a.) Hypothetical tetrahedral-dodecahedral “chain” that could be found in a Mg-Fe-Ca
684 intermediate composition garnet. Both O_4H_4 (H atoms are the pinkish-colored spheres) and SiO_4
685 (red) “tetrahedra” are shown. For example, in the case of a pyrope-rich solid-solution crystal, the
686 yellow spheres would represent Mg, brown Fe^{2+} and green Ca. b.) One hypothetical local divalent
687 X-cation environment around an O_4H_4 group in garnet. The oxygen anions from each of the four
688 OH^- dipoles form the central tetrahedron and they can be bonded locally to different combinations
689 of X-cations. This can lead to OH^- mode broadening in solid-solution crystals (see text).

690

691 Figure 7. IR spectra of $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (P-13 - Geiger et al., 1991) synthesized at $P(\text{H}_2\text{O}) = 2.3 \text{ Ga}$
692 and $T = 1100 \text{ }^\circ\text{C}$ and garnet of composition $(\text{Mg}_{2.50}\text{Fe}^{2+}_{0.59})(\text{Si}_{0.06}\text{Al}_{1.76}\text{Cr}_{0.08}\text{Fe}^{3+}_{0.02})\text{Si}_3\text{O}_{12}$
693 (spectrum MA384 digitized from Thomas et al., 2015, with absorbance divided by 30) synthesized
694 at $P(\text{H}_2\text{O}) = 18 \text{ GPa}$ and $T = 1800 \text{ }^\circ\text{C}$ (with $0.5 \text{ }\mu\text{L H}_2\text{O}$ added). The OH^- band defines a local
695 hydropyrope cluster in both crystals.

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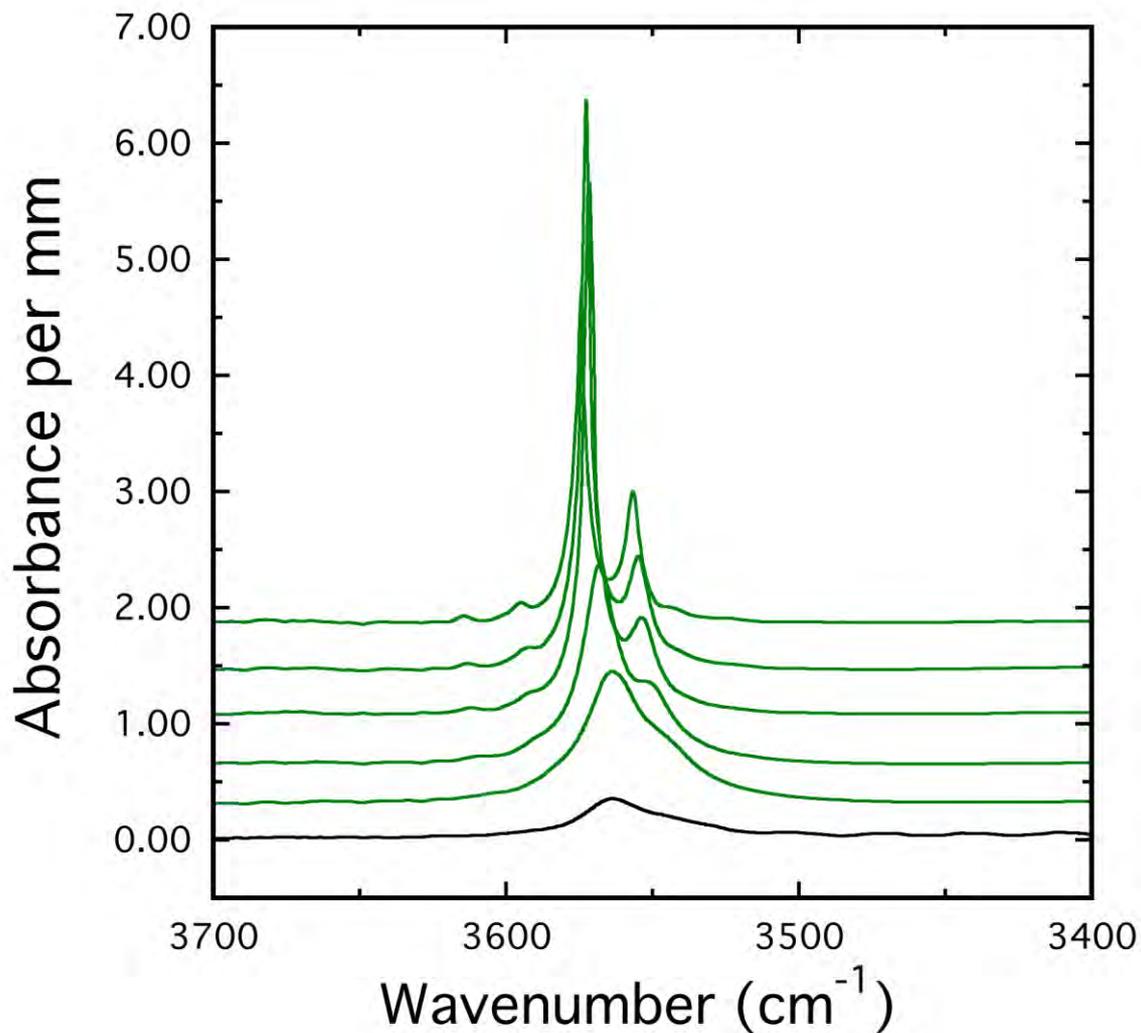
697 Figure 8. Comparison of IR spectra of two synthetic and three natural pyropes. The synthetic Ti-
698 bearing pyrope is from Geiger et al. (2000) and end-member pyrope from Geiger et al. (1991). The
699 IR spectra for the three natural pyropes are from Bell and Rossman (1992, note that the IR spectra
700 for RTF-2 and RTF-4 are interchanged in their work). The garnets show their three different

701 wavenumber types “high, middle and low” or the I, II and III groups of Matsuyk et al. (1998). The
702 three types or groups are marked by red, blue and green arrows, respectively. The red arrow marks
703 a possible local hydropyrope cluster in the garnet (about 3630 cm^{-1} in the synthetics and 3650 cm^{-1}
704 in the natural solid solution RTF-2). The blue arrow marks a possible hydrogrossular-like cluster
705 in RTF-4 and LAC-40 (at about 3570 cm^{-1}). The green arrow marks an OH mode possibly related
706 to the presence of Ti in garnet. See text for further discussion.

707
708 Figure 9. IR spectra of natural end-member spessartine (GRR-43 - 0.271 mm), natural end-
709 member pyrope (Masueria 2b - 2.308 mm) and pyrope synthesized from a gel (Py-27 in Geiger et
710 al., 1991, normalized to 5.0 mm). The latter has bands at 3663, 3651, 3641, and 3618 and a low
711 energy shoulder at 3604 cm^{-1} and also a weak shoulder on the high energy wing of the band at
712 3663 cm^{-1} .

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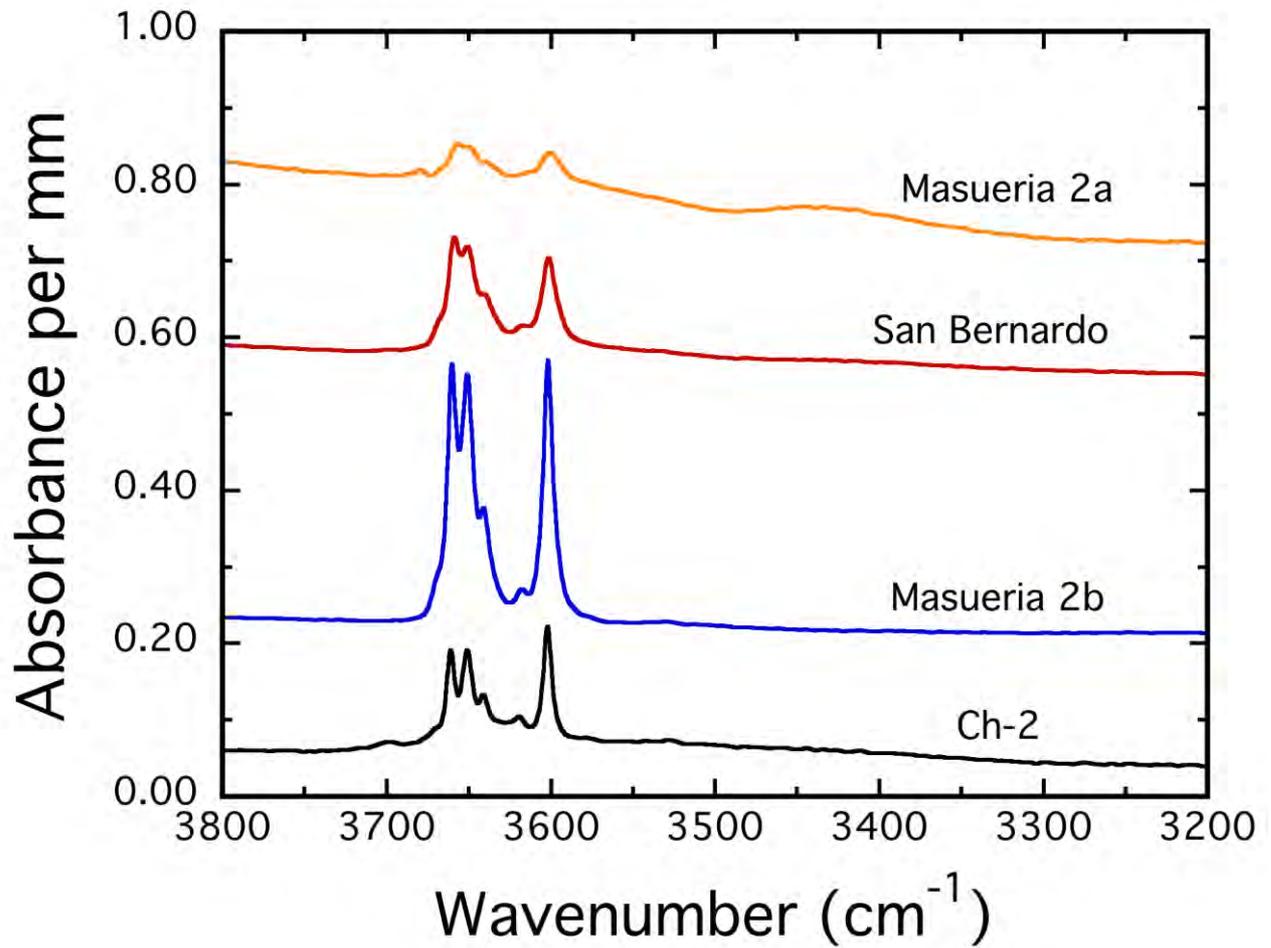
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Fig. 1

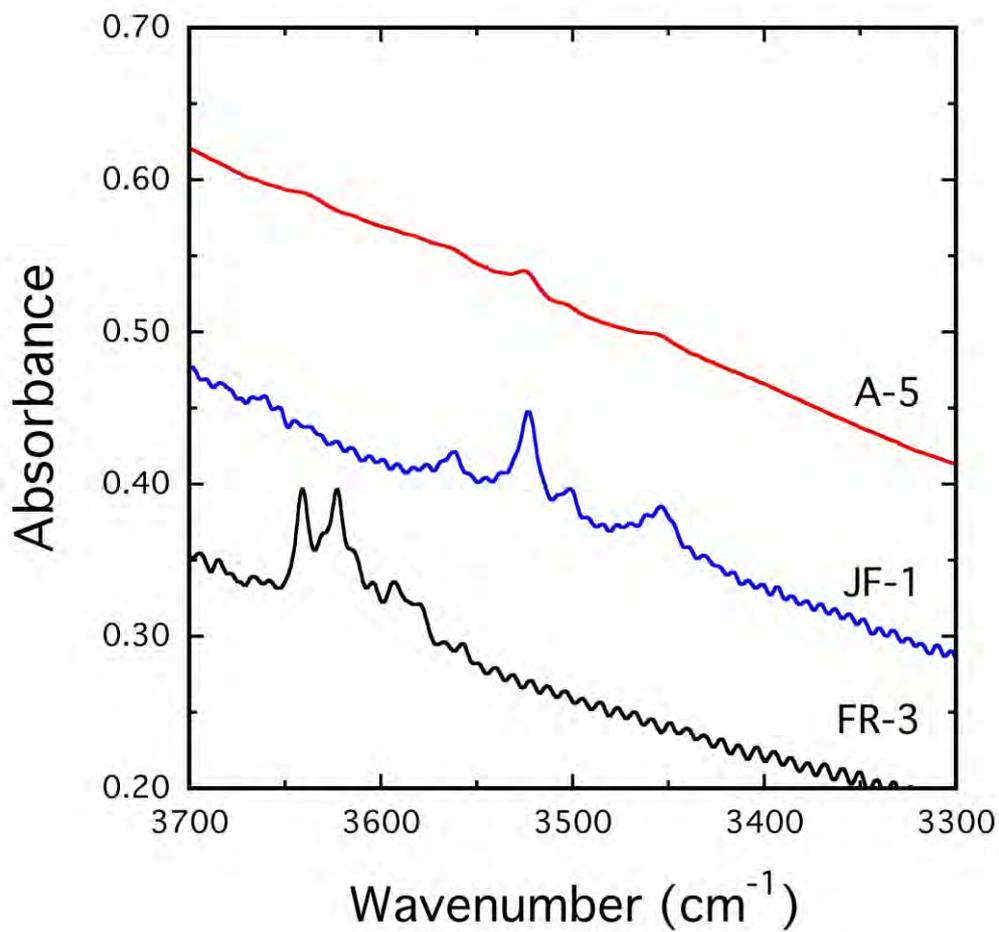
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Fig. 2

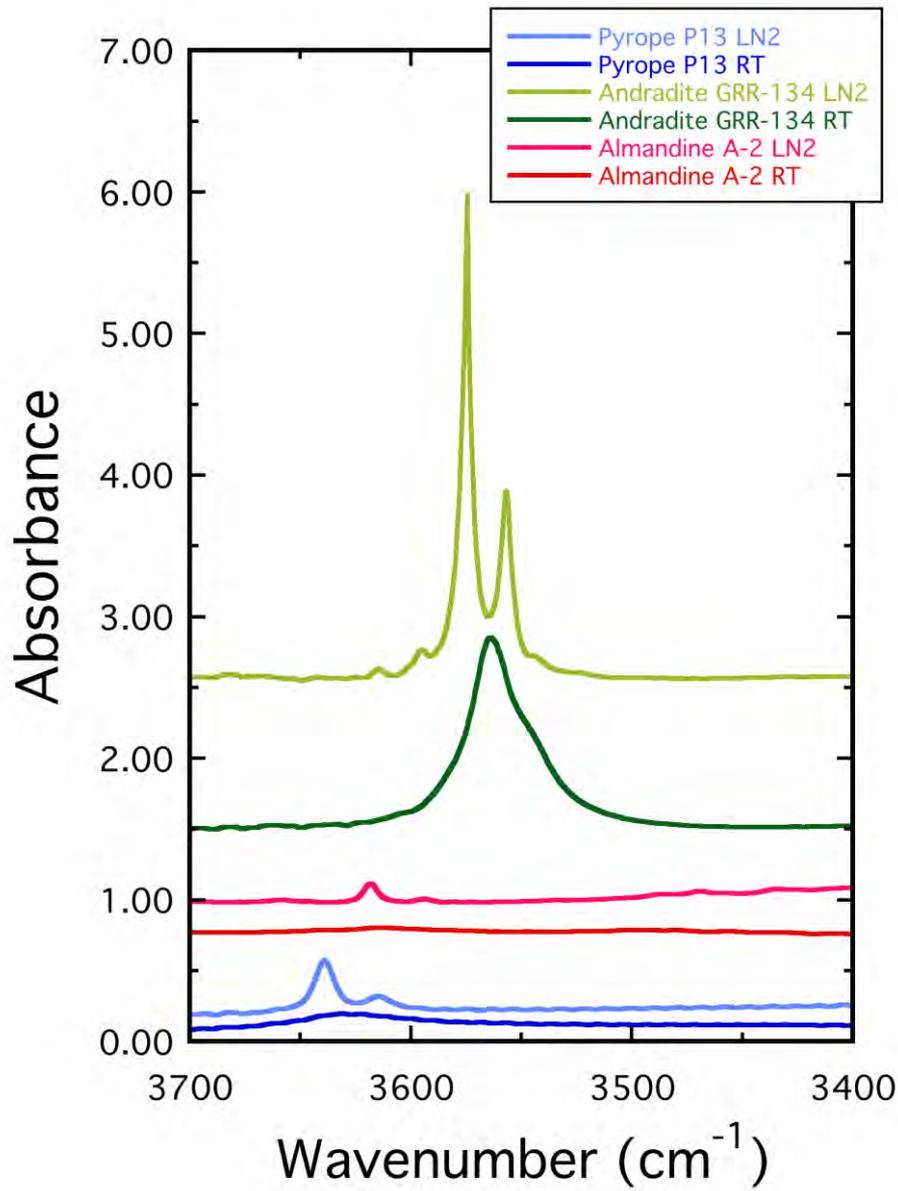
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Fig. 3

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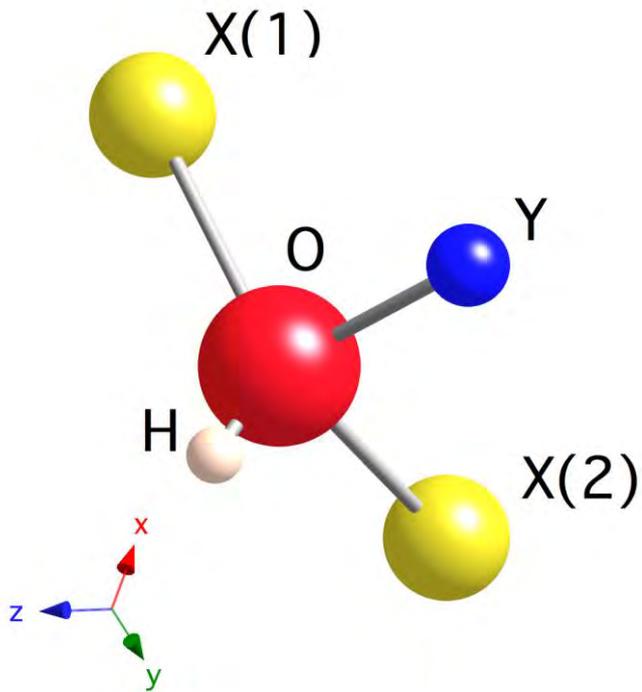


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Fig. 4

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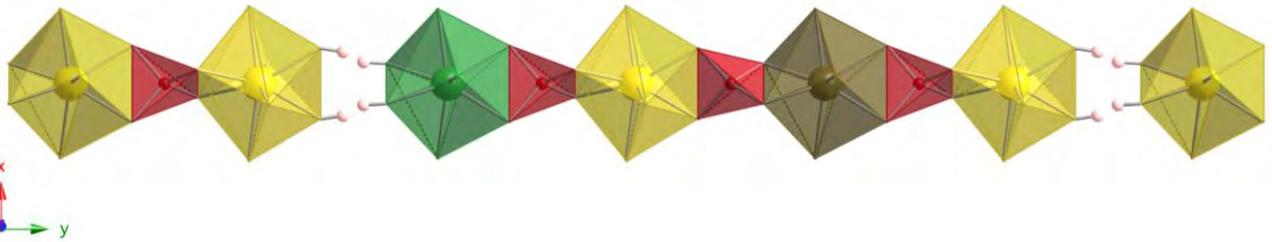
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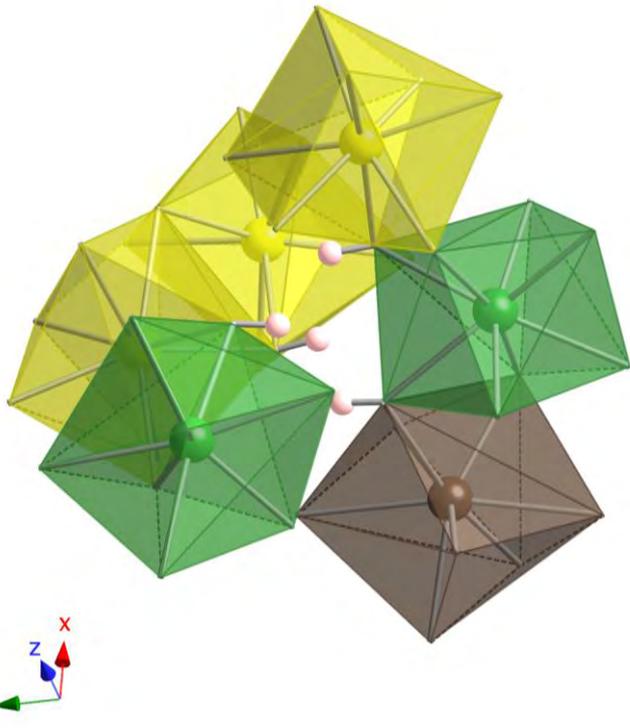
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Fig. 5

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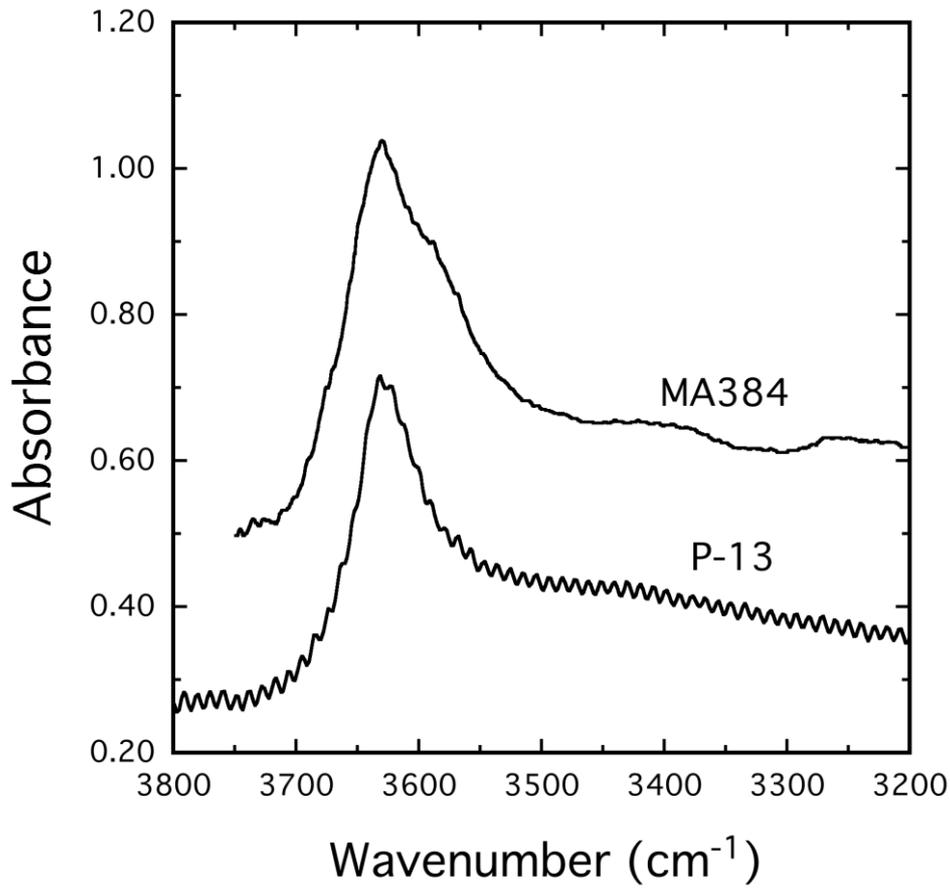


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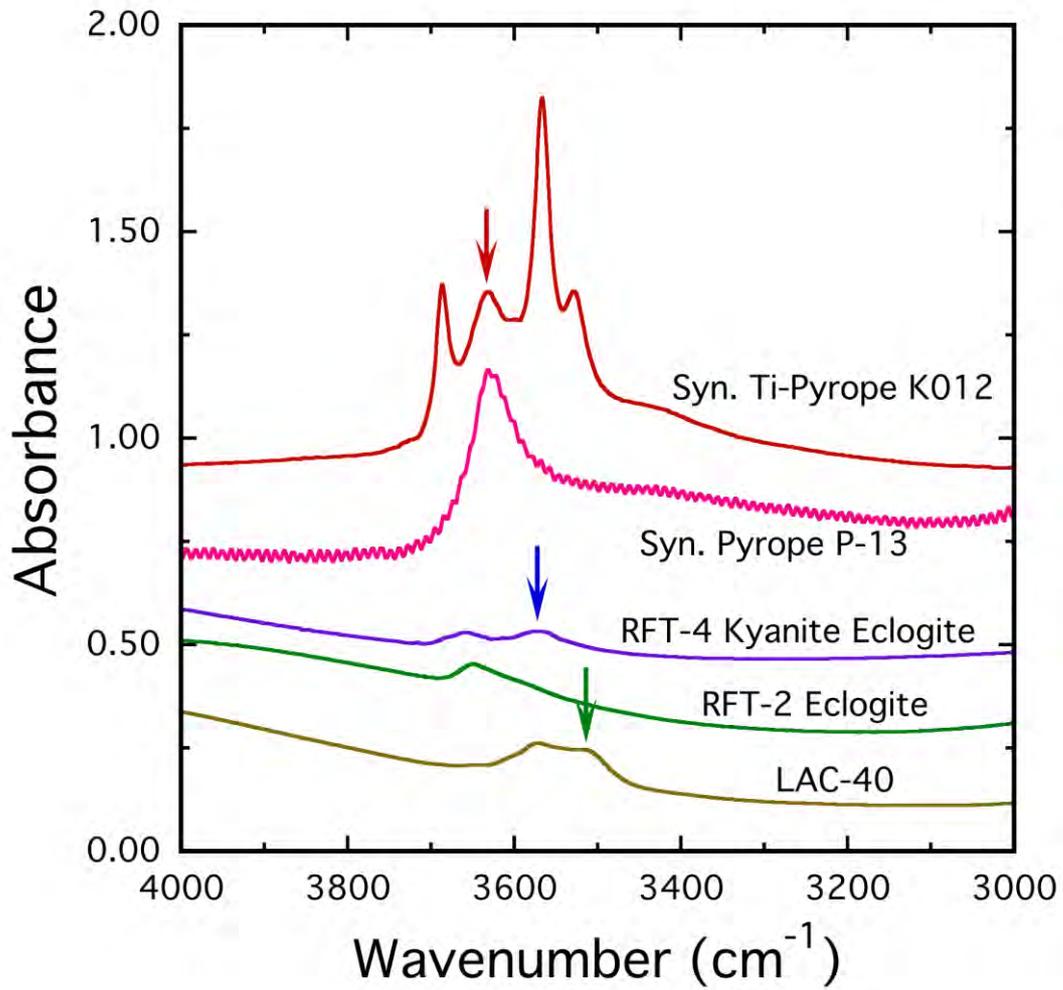
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Fig. 7

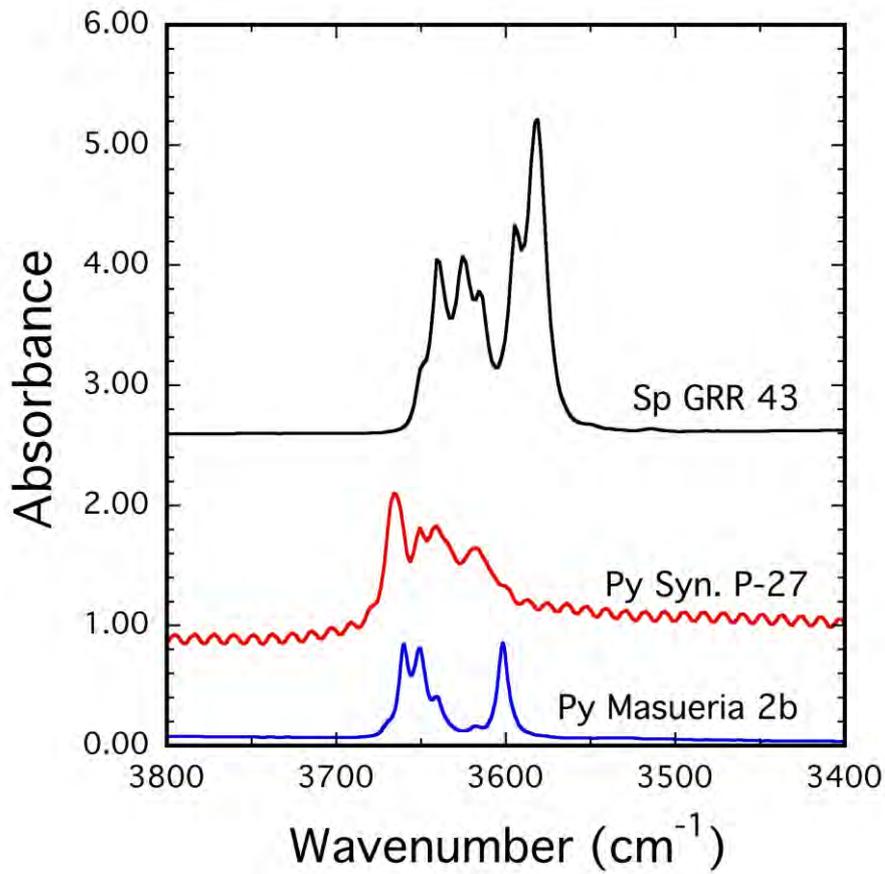
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Fig. 8

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Fig. 9