

1 Revision 2

2 **Water effects on the anharmonic properties of forsterite**

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18 **ABSTRACT**

19 In order to quantify the effects of hydration on anharmonicity of olivine
20 thermodynamics, we have measured *in situ* Raman spectra of an extremely hydrous
21 forsterite with 4500 ppm (wt) H₂O at temperatures up to 1273K. All the Raman modes
22 in hydrous forsterite shift linearly to lower wavenumbers with increasing temperature.
23 The calculated isobaric mode Grünesien parameters related to SiO₄ internal stretching
24 and bending vibrations are much lower than lattice vibrations. Additionally, compared
25 with anhydrous forsterite, except for the modes at 919, 858 and 227 cm⁻¹, water
26 greatly reduces the isobaric mode Grüneisen parameters of the Raman modes in
27 forsterite. Water also has a large effect on the anharmonic parameters related to lattice
28 vibrations whereas it has little effect on the anharmonic parameters related to SiO₄
29 internal stretching and bending vibrations. Those results have the implications to the

30 variations of local structure with temperature and estimation of water effects on the
31 thermodynamics of forsterite.

32 **Keywords:** water, anharmonic properties, Raman mode, forsterite

33 INTRODUCTION

34 Olivine is a major constituent of the upper mantle (Akimoto et al. 1976). It is
35 known to contain significant amounts of water as OH defects in the structure and can
36 be considered as a large reservoir of water in the upper mantle (Bell and Rossman
37 1992; Bolfan-Casanova 2005; Beran and Libowitzky 2006; Koch-Müller et al. 2006).
38 The presence of water in olivine has a profound influence on the physical properties
39 of olivine, thereby on the dynamics of the upper mantle (Hirth and Kohlstedt 1996;
40 Jung and Karato 2001; Mei and Kohlstedt 2000; Karato 2006; Wang 2010). Moreover,
41 water has great effects on structure and thermal expansion of olivine (Smyth et al.
42 2006; Ye et al. 2009). However, it is not clear whether water affects such
43 thermodynamic functions as heat capacity and entropy. Direct measurements of those
44 thermodynamic properties of the minerals under deep earth conditions are difficult
45 (Gillet et al. 1991; Gillet et al. 1997; Fujimori et al. 2002), so it is desirable to have
46 another method for estimating those properties. One of the important contributions of
47 vibrational spectroscopy is the calculation of those thermodynamic functions (Kieffer
48 1979).

49 The lattice anharmonicity refers to the vibrational effects that do not follow
50 simple harmonic motion. It is indispensable to understand such ubiquitous phenomena

51 as thermal expansion and thermal conductivity which can not be explained in a
52 harmonic system. Moreover, anharmonicity is especially remarkable and can
53 dramatically modify the thermodynamic properties of material at high temperature
54 (e.g., Karki et al. 2000; Wu 2015). So understanding anharmonic effects is one of the
55 current problems in physics and draws more and more interests from physicists and
56 geophysicists (e.g., Gillet et al. 1991; Gillet et al. 1997; Fujimori et al. 2002; Zucker
57 and Shim 2009; Deshpande et al. 2014; Silva et al. 2014; Sumita et al. 2014; Wu
58 2015). Since the mantle temperatures are expected to be higher than 1000 K, the
59 contribution of anharmonicity to thermodynamics of minerals of deep earth cannot be
60 neglected. As an Mg-end member of the olivine group - the main mineral in the upper
61 mantle, the anharmonic properties of dry forsterite was widely studied (Gillet et al.
62 1991; Reynard et al. 1992; Gillet et al. 1997). However, the anharmonicity of hydrous
63 forsterite has not yet been reported. In this study, we carry out *in situ* high temperature
64 Raman spectroscopic investigations on a hydrous forsterite to obtain the isobaric
65 mode Grüneisen parameters (γ_{iP}). Combined with the isothermal mode Grüneisen
66 parameters (γ_{iT}) and thermal expansion coefficient (α) of the hydrous forsterite of
67 the same batch reported by Ye et al. (2009) and Hushur et al. (2009), respectively, the
68 anharmonicities of hydrous forsterite can be calculated. Then, water effect on the
69 anharmonicities can be estimated compared with the data of dry forsterite (Gillet et al.
70 1991, which is consistent with their later paper Gillet et al. 1997).

71 **EXPERIMENTAL METHODS**

72 **Sample description**

73 The hydrous forsterite single crystal (SZ0410B) was synthesized at Bayerisches
74 Geoinstitut by Smyth et al. (2006). The synthesis was carried out in double-capsule
75 experiments in the 5000 ton multi-anvil press at 12 GPa and 1673 K. The water
76 content was measured by polarized FTIR spectroscopy on previously oriented grains
77 based on the calibration of Bell et al. (2003) and the sample SZ0410B contained 4505
78 ppm (wt) water (Smyth et al. 2006). The size of the crystal used in this study is about
79 150 μm .

80 **FTIR spectroscopy**

81 The Mid-IR spectra (2500 to 4000 cm^{-1}) of O-H stretching vibrations before and
82 after in situ high temperature Raman spectroscopic study were recorded (Fig. 1) to
83 check the retention of water during the heating process. The spectra were obtained
84 from a Nicolet 5700 FTIR spectrometer coupled with a Continuum microscope, using
85 a KBr beam-splitter and a liquid-nitrogen cooled MCT-A detector. All IR
86 measurements were carried out using transmission technique. A total of 128 scans
87 were accumulated for each spectrum at a 4 cm^{-1} resolution. The aperture size was set
88 as 50 \times 50 μm . Measurements were made under a continuous dry air flush.

89 ***In situ* high temperature Raman spectroscopy**

90 *In situ* high temperature unpolarized Raman spectroscopic investigation was
91 conducted by use of Dilor XY micro-Raman system, with the LABRAM-HR

92 spectrometer. The forsterite grain was placed on the sapphire window in a Linkam
93 TS1500 heating stage. The resistance heater was used to produce high temperature,
94 and an S type thermocouple was used to measure the sample temperature with the
95 uncertainties of less than 1 K. The automatic temperature control unit can be
96 programmed to set up the heating rate, desired temperature and hold time at a
97 temperature. The sample was heated from 20 to 100, 200 °C and then to 1000 °C at
98 50 °C interval with the heating rate of 25 °C/min. The sample was kept at every
99 temperature for 5 minutes to reach thermal equilibrium.

100 The frequency range for the spectra was 100-1200 cm^{-1} . The sample was excited
101 by the 514.5 nm green line of a Spectra Physics Ar ion laser. A 50* objective was used
102 to focus the incident laser light on the sample and collect the light. The diameter of
103 the focused laser light spot was about 10 μm . The spectrometer was calibrated using
104 single-crystal silicon as a reference.

105 **Data analysis**

106 Peakfit v4.12 software was used to analyze Raman spectra at various
107 temperatures. The obtained main frequencies and corresponding temperature
108 derivatives are listed in Table 1. The uncertainty in the frequency is usually less than
109 1-3 cm^{-1} as observed by performing multiple fits on the spectra.

110 **RESULTS AND DISCUSSION**

111 Figure 1 shows the absorptions of O-H stretching vibrations in forsterite before
112 and after high temperature Raman spectra measurement. The strong OH bands at 3613,
113 3579, 3566 and 3477 cm^{-1} still exist, while some weak OH bands at 3550, 3449, 3415,
114 3382 and 3359 cm^{-1} weaken or disappear, indicating that little dehydration occurs
115 during the short heating process. For the total absorbance, the variation of integral
116 absorbance from 3700 to 3100 cm^{-1} between the IR spectra before and after heating is
117 1.6%, suggesting little dehydration during the whole heating process. However, Ye et
118 al. (2009) reported dehydration-breakdown of hydrous forsterite at about 900K. The
119 dehydration at 900 K reported by Ye et al. (2009) was assumed from the abrupt
120 decrease in the length of b axis based on the XRD result. However, FTIR is very
121 sensitive to O-H vibration and can directly detect the variation of OH. The little
122 dehydration observed in this study based on the FTIR result can also be explained by
123 the diffusion of H in forsterite. Since the diffusion of H is very slow at low
124 temperature, we just consider the diffusion at temperatures between 600 to 1000°C.
125 Based on the site-specific diffusion rate of hydrogen in forsterite (Padrón-Navarta et
126 al. 2014), the preservation of water corresponding to the OH bands at 3613, 3579,
127 3566 and 3477 cm^{-1} was calculated up to 99% during this short heating process with
128 the heating rate of 25°C/min and the hold time of 5 min at each temperature. As a
129 result, it is not difficult to understand the preservation of the main OH bands at 3613,
130 3579, 3566 and 3477 cm^{-1} after the heating.

131 **Raman modes at room temperature**

132 It is known that in the forsterite structure, the M1 octahedron shares two edges
133 with SiO₄ tetrahedra, whereas the M2 octahedron shares only one edge with a SiO₄
134 tetrahedron. In view of the greater extent of edge sharing between SiO₄ and M1
135 polyhedra, it is expected that the M1 cation can greatly influence the SiO₄ internal
136 mode frequency. According to Smyth et al. (2006), the water is mainly incorporated in
137 M1 vacancies in this forsterite, thereby water is supposed to influence the SiO₄
138 internal mode frequency. However, from the Raman spectrum of the hydrous forsterite
139 at room temperature (Fig. 2), the Raman mode frequencies of this forsterite sample
140 with 4505 ppm (wt) water agree well with the results of anhydrous forsterite and
141 forsterite with 8900 ppm (wt) water (Gillet et al. 1991; Gillet et al. 1997; Kolesov and
142 Geiger 2004; Hushur et al. 2009; Makeown et al. 2010), indicating water has little
143 effect on the Raman mode frequencies at ambient conditions. For wadsleyite, Liu et al.
144 (1998) observed a lower frequency shift about 6 cm⁻¹ of most Raman modes in
145 wadsleyite with 2.5% water and Kleppe et al. (2001) observed new Raman modes in
146 wadsleyite with 1.65% water as compared with anhydrous wadsleyite. As a result, it is
147 probably because that the water content up to 8900 ppm (wt) is still not enough to
148 significantly affect the silicate framework lattice in forsterite at ambient conditions.

149 The lower frequencies ranging from 200 to 500 cm⁻¹ are Mg₂ displacements
150 mixed with SiO₄ translations and rotations (below we use the term “lattice vibrations”
151 to denote these low-frequency modes), the frequencies ranging from 500 to 700 cm⁻¹
152 are SiO₄ internal bending modes, whereas the higher frequencies ranging from 800 to
153 1200 cm⁻¹ are the SiO₄ internal stretching modes (Chopelas 1991; Kolesov and Geiger

154 2004; McKeown et al. 2010). The SiO₄ internal stretching modes at 968, 919, 858 and
155 825 cm⁻¹ at room temperature are much more intense than the other modes (Fig. 2).
156 Based on the selection rules of Raman spectroscopy, the incident light induces an
157 instantaneous dipole moment through deforming the electron cloud around the
158 molecule. The intensity of Raman mode depends on how easily the electron cloud can
159 be deformed, a property measured by the polarizability. So, the intensive SiO₄ internal
160 stretching modes suggest the highly polarizable oxygen environments.

161 **Variations of Raman modes with increasing temperature**

162 With increasing temperature, the Raman bands become broader, weaker and
163 overlapped (Fig. 2), resulting in the disappearance of the mode at 882 cm⁻¹ observed
164 at room temperature above 873 K. The evolution of the frequencies of the observed
165 modes with temperature is illustrated in Figure 3. It is obvious in Figure 3 that all the
166 modes shift linearly to lower wavenumbers with increasing temperature. The
167 temperature derivatives of the Raman frequency modes $\left(\frac{\partial \nu_i}{\partial T}\right)_P$ are listed in Table 1.
168 Among the three A_g modes of SiO₄ internal stretching vibrations in this hydrous
169 forsterite, the modes at 968 cm⁻¹ observed at room temperature display the highest
170 temperature dependences, in agreement with Gillet et al. (1991) and Gillet et al. (1997)
171 for anhydrous forsterite. Similarly, Hushur et al. (2009) reported that this mode in
172 hydrous forsterite showed the highest pressure dependence among the three high
173 frequency A_g modes of SiO₄ tetrahedra, in agreement with Chopelas (1991) for
174 anhydrous forsterite. Hushur et al. (2009) ascribed this higher volume dependence of

175 the mode at 968 cm^{-1} to the relatively shorter Si-O distance.

176 The temperature and pressure dependences of a given frequency (ν_i) result from
177 two contributions: a pure-volume contribution due to the compressibility and thermal
178 expansion; a pure-temperature and -pressure contribution arising from intrinsic
179 anharmonicity (Gillet et al. 1989; Fujimori et al. 2002). As a result, the following
180 expressions can be derived (Gillet et al. 1989; Fujimori et al. 2002; Okada et al.
181 2008):

$$182 \quad \gamma_{iT} = \left(\frac{\partial \ln \nu_i}{\partial \rho} \right)_T = \frac{K_T}{\nu_i} \left(\frac{\partial \nu_i}{\partial P} \right)_T, \quad (1)$$

$$183 \quad \gamma_{iP} = \left(\frac{\partial \ln \nu_i}{\partial \rho} \right)_P = \frac{1}{\alpha \nu_i} \left(\frac{\partial \nu_i}{\partial T} \right)_P, \quad (2)$$

$$184 \quad a_i = \left(\frac{\partial \ln \nu_i}{\partial T} \right)_V = -\alpha (\gamma_{iP} - \gamma_{iT}), \quad (3)$$

185 where ρ is the molar density, α is the thermal expansion coefficient, K_T is the
186 isothermal bulk modulus, γ_{iP} is the isobaric mode Grüneisen parameter, γ_{iT} is
187 isothermal mode Grüneisen parameter, and a_i is intrinsic anharmonic parameter.

188 Using the obtained temperature derivatives of the Raman frequency modes at
189 ambient pressure $\left(\frac{\partial \nu_i}{\partial T} \right)_P$ and the thermal expansion coefficient (α) of hydrous
190 forsterite reported by Ye et al. (2009), the isobaric mode Grüneisen parameters (γ_{iP})
191 of hydrous forsterite were calculated in Table 1 based on formula (2). Figure 4
192 displays the calculated isobaric mode Grüneisen parameters for various Raman
193 frequency modes. It is evident in Figure 4 that the lattice vibration modes, especially
194 the mode at 305 cm^{-1} related to Mg2 translation, have higher γ_{iP} values than SiO_4

195 internal stretching and bending modes, which is in accordance with the results of
196 anhydrous forsterite reported by Gillet et al. (1991) and Gillet et al. (1997). This
197 indicates that $\text{Mg}(2)\text{O}_6$ octahedron has a higher thermal expansibility than SiO_4
198 tetrahedron in the hydrous as well as anhydrous forsterite, which is also consistent
199 with the results of X-ray diffraction at different temperatures of anhydrous forsterite
200 reported by Smyth and Hazen (1973). Comparing our data with those for anhydrous
201 forsterite (Table 1 and Fig. 5), except for the modes at 919, 858 and 227 cm^{-1} , water
202 reduces the isobaric mode Grüneisen parameters of the Raman modes in forsterite.
203 The effect of water on the lattice modes is slightly larger for the comparison to Gillet
204 et al. (1991) than to Gillet et al. (1997). Therefore, water appears to influence the
205 framework lattice modes of forsterite at high temperature. It can also be concluded
206 from this study that water makes the $\text{Mg}(2)\text{O}_6$ octahedron less expansive. Ye et al.
207 (2009) reported that 0.89% water increase thermal expansion coefficient of anhydrous
208 forsterite from 36.4 to 38.1 (10^{-6} K^{-1}). The reason may be that water makes $\text{Mg}(1)\text{O}_6$
209 octahedron more expansive, which deserves to be tested in future by investigating
210 water effects on the structure of forsterite at varying temperatures.

211 Combined with the present isobaric mode Grüneisen parameters, isothermal
212 mode Grüneisen parameters (Hushur et al. 2009) and thermal expansion coefficient of
213 hydrous forsterite (Ye et al. 2009), intrinsic anharmonic mode parameters of hydrous
214 forsterite, a_i , were calculated from formula (3) and listed in Table 1. Consistent with
215 anhydrous forsterite (Gillet et al. 1991, Gillet et al. 1997), the intrinsic anharmonicity
216 has a negative sign in the hydrous forsterite for most modes except for the mode at

217 610 cm^{-1} . However, the a_i values of the majority of Raman modes are generally
218 greater in magnitude in the hydrous forsterite than the anhydrous one with the
219 exception of the modes at 825 and 437 cm^{-1} , indicating the water has distinctive effect
220 on intrinsic anharmonicity of different mode. Figure 6 compares the intrinsic
221 anharmonic parameters of hydrous forsterite of this study and anhydrous forsterite
222 reported by Gillet et al. (1991). It is obvious that (1) the absolute values of intrinsic
223 anharmonic parameters related to SiO_4 internal stretching and bending vibrations are
224 similar for both hydrous and anhydrous forsterite; (2) water has large effects on the
225 magnitudes of anharmonic parameters related to lattice vibrations.

226 **IMPLICATIONS**

227 We have used *in situ* Raman spectra up to 1273 K to investigate the water effects
228 on the isobaric mode Grünesien parameters and intrinsic anharmonicities of the
229 forsterite. The results indicate that water can influence framework lattice modes of
230 forsterite at high temperature, and the magnitudes of anharmonic parameters related to
231 lattice vibrations. Taking the three lattice modes at 437, 305 and 227 cm^{-1} into account,
232 the absolute values of anharmonic parameters are, on average, higher by about
233 $0.4 \cdot 10^{-5} \text{ K}^{-1}$ than those for anhydrous forsterite (Gillet et al. 1991). As stated above,
234 anharmonicity must be considered in the case of calculation of thermodynamic
235 functions at high temperature. Taking the calculation of isochoric heat capacity as an
236 example, the isochoric heat capacity with the anharmonic contribution is

$$237 \quad C_v = 3 nR \sum_{i=1}^m C_{vi}^h (1 - 2a_i T) \quad (4)$$

238 where C_v^h is the harmonic part of the heat capacity, while the $-3nRT \sum_{i=1}^m 2a_i C_{vi}^h$ is
239 the contribution of the anharmonic properties. In the high-temperature limit ($C_{vi} \approx kT$),
240 at which anharmonic effects become significant, formula 4 becomes
241
$$C_v = 3nR C_v^h (1 - 2a_{average} T) \quad (5)$$

242 where $a_{average}$ is the arithmetic mean of the anharmonic parameters. Because the
243 average anharmonic parameters of the three lattice modes for hydrous forsterite about
244 $0.4 \cdot 10^{-5} \text{K}^{-1}$ lower than for the anhydrous forsterite, the C_v corrected by the
245 anharmonic effects of the lattice vibrations is 11% higher than for anhydrous forsterite.
246 However, taking the mean anharmonic parameters of all the modes into account,
247 there's little difference of C_v between hydrous and anhydrous forsterite.

248 Although natural olivines contain relatively little water (e.g., Bell and Rossman
249 1992; Peslier et al. 2002; Bell et al. 2004), these low water contents may not represent
250 the source region because of the rapid hydrogen diffusion through olivine at high
251 temperature especially for hydrogen incorporated in M vacancies in olivine
252 (Demouchy et al. 2006; Padrón-Navarta et al. 2014). Numerous experiments at high
253 temperature and pressure showed that olivine can contain considerably more water
254 even up to 8900 ppm (wt) (Kohlstedt et al. 1996; Mosenfelder et al. 2006; Smyth et al.
255 2006; Férot and Bolfan-Casanova 2012). According to the previous high pressure
256 Raman spectroscopic studies on hydrous and anhydrous wadsleyite (Chopelas 1991;
257 Liu et al. 1994; Liu et al. 1998; Kleppe et al. 2001; Yang et al. 2012), the γ_{IT}
258 parameters are similar between hydrous wadsleyite samples with different water
259 contents, while they are different from those of anhydrous wadsleyite. As a result,

260 water rather than its content is significant to influence the anharmonicity of
261 wadsleyite. It maybe suitable for forsterite, but accurate relationship between water
262 content and the anharmonicity of olivine still should be measured to apply to the real
263 deep mantle.

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413 **Table 1** Frequencies of Raman modes, corresponding temperature derivatives,
 414 isobaric mode Grüneisen parameters and intrinsic anharmonic parameters of hydrous
 415 and anhydrous forsterite.

Symmetry	ν_i (cm^{-1})	$\left(\frac{\partial \nu_i}{\partial T}\right)_P$ (cm^{-1}/K)	hydrous		anhydrous		Mode assignment
			γ_{iP}	$a_i(10^{-5}\text{K}^{-1})$	γ_{iP}^*	$a_i(10^{-5}\text{K}^{-1})^*$	
A_g	968	-0.033	0.89	-1.16	1.07	-1.07	$\text{SiO}_4 \nu_3$
B_{3g}	919	-0.034	0.97	/	0.82	-1.16	$\text{SiO}_4 \nu_3$
A_g	858	-0.023	0.70	-1.04	0.72	-0.60	$\text{SiO}_4 \nu_3 + \nu_1$
A_g	825	-0.022	0.70	-0.45	0.79	-0.81	$\text{SiO}_4 \nu_3 + \nu_1$
A_g	610	-0.012	0.52	0.81	0.82	-0.31	$\text{SiO}_4 \nu_4$
B_{3g}	590	-0.016	0.71	-0.87	0.85	-0.50	$\text{SiO}_4 \nu_4$
B_{3g}	437	-0.026	1.56	-0.19	2.52	-2.38	$\text{SiO}_4 r^\#;$ $\text{SiO}_4 \nu_2 + \nu_2$
A_g	418	-0.027	1.70	/	2.04	-2.74	$\text{SiO}_4 \nu_2$
A_g	305	-0.031	2.67	-5.18	2.87	-3.22	$M2 t^\#$
A_g	227	-0.016	1.85	-4.42	1.82	-3.00	$\text{SiO}_4 t;$ $\text{SiO}_4 t + M2$

416 Note: * data from Gillet et al. (1991); # r and t indicate rotation and translation, respectively.

417 γ_{iP} : corresponding to the values at 294K, calculated following the expressions $\gamma_{iP} =$

418 $\frac{1}{\alpha \nu_i} \left(\frac{\partial \nu_i}{\partial T}\right)_P$, where α is the thermal expansion coefficient.

419 a_i : calculated following the expressions $a_i = \alpha (\gamma_{iT} - \gamma_{iP})$, where α is the thermal expansion
 420 coefficient.

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425 **Figure Captions**

426 FIGURE 1. FTIR spectra of the forsterite before and after high temperature Raman
427 spectra measurements. The OH bands weakening or disappearing during the heating
428 process are labeled.

429 FIGURE 2. In situ Raman spectra of forsterite up to 1273 K from 100-1200 cm⁻¹.

430 FIGURE 3. Evolutions of Raman mode frequencies of forsterite with increasing
431 temperature for two frequency ranges: a), 100-700 and b), 700-1200 cm⁻¹). Solid
432 symbols and lines are for hydrous forsterite, while open symbols and dashed lines are
433 for anhydrous forsterite (Gillet et al. 1991).

434 FIGURE 4. Isobaric mode Grüneisen parameters for various Raman mode frequencies
435 in forsterite.

436 FIGURE 5. Relative changes of isobaric mode Grüneisen parameters as compared to
437 anhydrous forsterite, which is determined by the expression $\left(\frac{\gamma_{iPhydrous} - \gamma_{iPanhydrous}}{\gamma_{iPanhydrous}} \right)$,

438 where the data for anhydrous forsterite are from Gillet et al. (1991) and Gillet et al.
439 (1997).

440 FIGURE 6. Intrinsic anharmonic parameters for various Raman mode frequencies in
441 hydrous and anhydrous forsterite.

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