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1 Hydrogen, trace, and ultra-trace element
2 distribution in natural olivines

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4
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25 **Abstract**

26 We investigate the coupling between H, minor, trace, and ultra-trace element incorporations in
27 17 olivines from ten different locations covering various petrological origins: magmatic,
28 hydrothermal and mantle-derived context. Concentrations in major element are determined by
29 micro X-ray fluorescence. Minor, trace, and ultra-trace element are determined by laser ablation
30 inductively coupled plasma mass spectrometry. Hydrogen concentrations are quantified using
31 unpolarized and polarized Fourier transform infrared spectroscopy (FTIR). Forsterite contents
32 (83.2 to 94.1 %) reflect the petrogenetic diversity. Hydrogen concentrations range from 0 to 54
33 ppm H₂O wt. Minor element concentrations (Ni + Mn) range from 3072 to 4333 ppm, and
34 impurities are dominated by Ni, Mn, Ca or B. Total trace element concentrations range from
35 8.2 to 1473 ppm. Total rare Earth and extended ultra-trace elements concentrations are very
36 low (< 0.5 ppm). Magmatic and hydrothermal olivines show the most and least amount of
37 impurities, respectively, and mantle-derived olivines have concentrations between these two
38 extremes. Combined with minor, trace, and ultra-trace element concentrations, the hydrogen
39 concentrations and FTIR OH bands reflect the point defect diversity imposed by different
40 geological settings. Hydrogen concentrations are inversely correlated with divalent impurities,
41 indicating their competition for vacancies. However, a broad positive correlation is also found
42 between OH bands at 3575 and 3525 cm⁻¹ and Ti, confirming the existence of Ti-clinohumite-
43 like point defect in mantle olivines. Nonetheless, Ti does not exclusively control hydrogen
44 incorporation in olivine due to the co-existence with other mechanisms, and its effect appears
45 diluted. Our results confirm that hydrogen behaves as a peculiar incompatible element, and
46 furthermore as an opportunistic impurity in olivine.

47

48 **Key words:** Olivine, hydrogen, minor elements, trace elements, FTIR, LA-ICP-MS.

49

50 **1. Introduction**

51 Above absolute zero temperature, perfect minerals do not exist, all minerals contain
52 assorted atomic-scale defects in various amounts, and mostly ionic vacancies. The
53 concentration and mobility of these defects increases significantly with increasing temperature
54 (e.g., Schmalzried, 1981; Philibert, 1995; Schwartz and Lang, 2016). Furthermore, the
55 vacancies in olivine can incorporate a large range of atomic impurities covering the entire
56 chemical classification from heavy (U, Th) to light elements (H, Li, He) in ppb- to ppm-level
57 concentrations (e.g., Bell and Rossman 1992; Sykes et al. 1994; Ingrin and Skogby 2000; Kent
58 and Rosmann 2002; Burnard et al. 2015; Tollan et al. 2018; Delon et al. 2018, 201; Bussweiler
59 et al. 2019, Rasmussen et al., 2020). The atomic impurities are embedded in the crystalline
60 structure of olivine following the substitution rules from Goldschmidt's (Goldschmidt 1926;
61 Ringwood 1955; Kröger and Vink 1956), and more complex coupled substitutions can occur
62 with increasing nonstoichiometry (e.g., Nakamura and Schmalzried 1983; Jurewicz and Watson
63 1988a, b; Berry et al., 2007a; Padrón-Navarta et al. 2014; Tollan et al. 2018). Olivine is the
64 most depleted upper mantle mineral in trace elements, thus containing significantly less trace
65 elements than in co-existing pyroxenes or garnets (e.g., Bodinier et al. 1987; Bodinier and
66 Godard 2014; Satsukawa et al. 2017; Garrido et al. 2000), therefore olivine is not the most
67 important trace element reservoir in the Earth's upper mantle. However, olivine is the most
68 abundant (>60%) and the only interconnected mineral in the uppermost mantle, implying that
69 its rheological properties control both the viscosity of lithospheric plates and the underlying
70 convecting asthenosphere. As the viscosity of olivine-rich rock might decrease with increasing
71 incorporation of impurities such as H, Fe or Ti (e.g., Mackwell et al. 1985; Mei and Kohlstedt
72 2000; Demouchy et al. 2012; Faul et al. 2016; Tielke et al. 2017), the mechanisms of hydrogen
73 incorporation in olivine has been the focus of many experimental studies (e.g., Mackwell and
74 Kohlstedt 1990; Bai and Kohlstedt 1992; Kohlstedt et al. 1996; Kohlstedt and Mackwell 1998;

75 Mosenfelder et al. 2006; Withers and Hirschmann 2008; Férot and Bolfan-Casanova 2012;
76 Padrón-Navarta and Hermann 2017) for various thermodynamic conditions (e.g., pressure,
77 temperature, f_{O_2} , f_{H_2O} , a_{SiO_2} , e.g., Kohlstedt et al. 1996; Gaetani et al. 2014) and chemical
78 composition (e.g. Ti, Al, Cr, etc; Berry et al. 2007a, Tollan et al. 2019). The most recent
79 experimental approaches include doping olivine with a high amount of atomic impurity before
80 or synkinetic with hydration (e.g., Tollan et al. 2019). While these experiments highlight the
81 individual mechanism of H incorporation, these results are not always directly applicable to
82 Earth's upper mantle.

83 The experiments on hydrogen incorporation were completed by studies of natural
84 mantle-derived olivine specimens (e.g., Beran and Zemman 1983; Bell and Rossman 1992;
85 Berry et al. 2005, 2007b; Beran and Libowitzky 2006; Skogby 2006; Peslier 2010; Demouchy
86 and Bolfan-Casanova 2016; Xia et al. 2017) and several seminal publications have provided
87 valuable spectral databases (Miller et al. 1987; Mosenfelder et al. 2006; G.R. Rossmann,
88 <http://minerals.gps.caltech.edu>, or the PULI database, <http://puli.mfgi.hu>).

89 Despite these advances, data available on trace element incorporation in mantle-derived
90 olivine are scarce and hinders our understanding and thus prediction ability on the mobility of
91 trace elements in olivine (e.g., Demouchy et al. 2006; Mosenfelder et al. 2006; Padrón-Navarta
92 et al. 2014; Thoraval and Demouchy 2014; Satsukawa et al. 2017; Thoraval et al. 2019). Indeed,
93 the coupling of co-existing atomic impurities in olivine were often neglected, principally due
94 to technical limitations (e.g., sample preparation and mass spectroscopy detection limits; see
95 Batanova et al. 2015, 2019; Zhang et al. 2016; Bussweiler et al. 2019). However, recent
96 analytical breakthroughs have sparked and renewed interest in coupled interactions between
97 trace elements in olivine (e.g., De Hoog et al. 2010; Spandler and O'Neill 2010; Foley et al.
98 2013; Bussweiler et al. 2015; 2019; Veter et al. 2017; 2019; Neave et al. 2018). Here we assess
99 the complex point defect diversity in natural olivines by characterizing the coexistence of

100 hydrogen with minor, trace, and ultra-trace elements. To explore a broad range of chemical
101 compositions, we selected olivines from various geological settings.

102

103 **2. Materials and Methods**

104

105 *2.1 Olivine specimens and sample preparation*

106

107 We selected 17 single-crystal olivines from ten different geological settings; most
108 specimens are from peridotite xenoliths that originated in the uppermost mantle (Table 1).
109 Three samples (harzburgite SAS20, high temperature (HT) harzburgite SAS21, lherzolite
110 SAS41) are spinel-bearing peridotites from Malaita (Ontong-Java Plateau; Demouchy et al.
111 2015) which contain olivines with low Al and different Ca contents. Samples SC and SC2018
112 are both San Carlos olivines (Arizona, USA), and LAZ is from Lanzarote (Canary Islands);
113 they are all from spinel-bearing peridotites. DMP2 and DMP4 are olivines from spinel-bearing
114 peridotites from Damaping (China). Specimen PA3 was extracted from a garnet-bearing
115 lherzolite from Pali-Aike (Chile; Demouchy, 2004) and OLM is from a very coarse-granular
116 peridotite from Olmani (Tanzania; OL10 from Baptiste et al. 2015). We have selected one
117 magmatic olivine (LR) from La Réunion (Indian Ocean). SAP is a large hydrothermal gem-
118 quality olivine from Sapat (Pakistan; see Göse et al. 2010), and samples HS and PP are from
119 the same locality but were not produced by hydrothermal processes; they are of mantle origin.
120 MYA is a hydrothermal olivine gem from Myanmar (Harlow et al. 2014). We completed the
121 data set with two centimetric gem-quality crystals (NW1 and NW2) from a metamorphosed
122 alpine-type peridotite massif in Norway; based on their chemical compositions, they are
123 hydrothermal specimens from Sandvika (see Medaris 1984) or Almoklovdalen (see Kent and
124 Rosmann 2002; Mosenfelder et al. 2006; Göse et al. 2008; their sample CIT15089 has Fo% =

125 93.51 – 93.76; Mosenfelder, person. comm. 14/01/2019). Samples NW1, NW2, SAP, and MYA
126 result from hydrothermal recrystallization in dunitic domains.

127 Samples were optically inspected to discard crystal sections containing macroscopic and
128 mesoscopic imperfections (e.g., spinel inclusions, lily pads, cracks, or milky or brownish
129 zonations; e.g., Mosenfelder et al. 2006). Each olivine was then cut into a millimetric right
130 prism with a rectangular base prior to *in-situ* chemical analyses. All faces of each prism were
131 hand-polished using a polishing jig and diamond-lapping films with grit sizes ranging from 30
132 to 1 μm . The final prepared size of each olivine prism is reported in Table 1 and photographs
133 are provided in Figure S1.

134 The distribution of major and a few minor elements were determined by micro X-ray
135 fluorescence (μXRF), hydrogen concentrations by polarized and unpolarized Fourier-transform
136 infrared spectroscopy (FTIR), and minor, trace/ultra-trace element concentrations by laser
137 ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Since LA-ICP-MS is a
138 destructive method, FTIR analyses were performed first, μXRF mapping second, and LA-ICP-
139 MS last. The analytical procedures are detailed in the same order in the following subsections.
140 The olivine crystals were free of any glue for FTIR analyses, then were fixed on a glass section
141 with crystal bond for both μXRF and LA-ICP-MS measurements.

142 We emphasize that all analyses per sample were performed on the same olivine prism,
143 and not on different olivine crystals co-existing in the same xenolith/hydrothermal vein, as
144 commonly done in other studies. Past practices were constrained by analytical requirements
145 and sample preparation and lead to none negligible scatter in the data. Our approach is designed
146 to investigate consistently the control of olivine crystal chemistry on hydrogen incorporation.

147

148 *2.2 Fourier-transform infrared spectroscopy*

149

150 We analyzed hydroxyl groups in olivine using transmission FTIR spectroscopy at the
151 Laboratoire Charles Coulomb (University of Montpellier, France). Unpolarized and polarized
152 infrared spectra were acquired using a Bruker IFS66v equipped with a liquid nitrogen-cooled
153 MCT detector (Mercatel alloy, HgCdTe), a KBr/Ge beam splitter, and coupled to a Bruker
154 HYPERION microscope. The infrared beam was polarized with a KRS-5 polarizer (thallium-
155 bromide-iodide) placed between the mid-IR source and the sample. Unpolarized IR
156 measurements were performed following the protocol of Denis et al. (2015). Optically clean
157 areas were chosen for analyses, and 256 scans were accumulated at a resolution of 4 cm^{-1} using
158 a square aperture ($100 \times 100\ \mu\text{m}$). Each spectrum was baseline corrected and the absorbance
159 normalized to 1 cm thickness. Each sample was washed several times in high purity acetone
160 prior to FTIR analyses and placed on a CaF_2 plate when necessary (i.e., for the smallest
161 samples). A minute amount of Fluorolube (ThermoScientific™) was used to eliminate
162 thickness fringes if needed. The olivine prisms were not crystallographically oriented (except
163 PA3). Still we acquired polarized and unpolarized FTIR spectra along three orthogonal
164 directions, compiling two triplets of polarized spectra and one triplet of unpolarized spectra for
165 each olivine prism (all spectra triplets are provided in supplementary material in Figure S2).
166 Since NW1 and SAS20 olivine specimens were large, FTIR profile were also acquired and are
167 provided in Figure S3.

168 Two types of IR calibrations were used to calculate hydrogen concentrations: the
169 frequency-dependent calibration of Paterson (1982) and the mineral-dependent calibration for
170 olivine of Withers et al. (2012). Hydrogen concentrations were calculated by integrating each
171 spectrum over the $3620 - 3050\text{ cm}^{-1}$ wavenumber range. This calibration allows a detection
172 limit of about 1 ppm of H_2O by weight (wt) for a 1mm-thick olivine sample, although the
173 estimated error from the empirical calibration of Paterson (1982) is around 30 % of the resulting
174 H concentration (e.g., Paterson 1982; Rauch 2000). Reported hydrogen concentrations are the

175 average of the three orthogonal unpolarized spectra or the three polarized spectra of each
176 orthogonal triplet from each olivine prism. Following the recommendations of Withers et al.
177 (2012) for unpolarized FTIR measurements of olivine, the maximum linear absorption of non-
178 normalized spectra did not exceed 0.3. Hydrogen concentrations are given in ppm H₂O wt., in
179 ppm of H (equals to molar concentration), and in H/10⁶Si to ease comparison with past studies.
180 Finally, the normalized integrated absorption area for use in future mineral-dependent IR
181 calibrations are provided in Table S1. Several spectra necessitated deconvolution to obtain the
182 integrated absorption area per peak. The best deconvolution results (i.e., the lowest residue
183 obtained for input peak positions as listed in Table 1 with ± 20 cm⁻¹, and using a gaussian
184 function) are provided in Figure S4 for samples LR, LAZ, PA3, SAS20 and SAS41.
185 Corresponding results of the deconvolution per mechanism of hydrogen incorporation (i.e.,
186 integrated normalized absorptions and relative % compare to bulk hydrogen) are compiled in
187 Table S2.

188

189 *2.3 X-ray fluorescence*

190 Major and minor element distributions within each olivine prism were measured by
191 μ XRF at the Department of Earth and Planetary Sciences (Macquarie University, Australia)
192 using a Bruker M4 Tornado. Because μ XRF does not require extensive sample preparation or
193 coating, this technique was preferred over electron microprobe measurements. Furthermore, the
194 polish quality required for FTIR analyses (final mirror polish with <0.5 μ m grid) is more than
195 sufficient for such μ XRF measurements. Analyses were performed at 50 kV and 200 μ A under
196 low vacuum (18 mbar). To detect compositional variability, all maps were acquired over the
197 entire sample with spot and step sizes of 20 μ m. Acquisition durations ranged from 4 to 32 min
198 depending on the size of the crystal. Twelve elements were analyzed: Si, Ti, Al, Cr, Fe, Mn,
199 Mg, Ca, Na, Ni, Co and Zn. To obtain quantitative estimates, the spectra were calibrated against

200 an in-house standard (SCO-2 San Carlos olivine). The μ XRF data compare well (i.e., within
201 errors) with electron microprobe measurements (see Table S3).

202

203 *2.4 Laser ablation inductively coupled plasma mass spectrometry*

204

205 Trace element analyses were performed on olivine samples by LA-ICP-MS at
206 Macquarie GeoAnalytical (Department of Earth and Planetary Sciences, Macquarie University,
207 Australia) using an Agilent 7700cs quadrupole ICP-MS system. The ICP-MS is coupled with
208 an automated laser ablation platform (Analyte G2, Photon Teledyne) equipped with a 2-volume
209 HelEx cell and housing an ArF 193 nm laser. Measurements were conducted in a He
210 atmosphere (total He flow of ~ 0.8 L min^{-1}), which enhances sensitivity and reduces inter-
211 element fractionation. Numerous studies have investigated the use of additional trace gases
212 such as H_2 , N_2 , or CH_4 (e.g., Guillong and Heinrich 2007; Hu et al. 2008; Scheffler and Pozebon
213 2014). Here, our in-house experiments agree with Guillong and Heinrich (2007) that the
214 addition of a few mL min^{-1} of H_2 (not N_2) increases the sensitivity for most elements by a factor
215 of 2 to 4 (see also Veter et al. 2019). Thus, given the expected low trace element concentrations
216 of olivine, 5 mL min^{-1} of H_2 was added to the central line (i.e., between the ablation cell and
217 the plasma torch). The H-bearing He gas stream and particles from the sample were finally
218 mixed with Ar ($\sim 0.90 \pm 0.02$ L min^{-1}) before entering the plasma with a final 30 mL mixed
219 volume. Signals were measured in time-resolved acquisition mode and each analysis lasted 300
220 s, separated by 40 s pauses between analyses. Analysis times comprised 220 s for background
221 (i.e., with the laser off), 60 s for mineral analysis (i.e., with the laser on), and 20 s for wash-out
222 monitoring. The laser was fired at an energy density of 7.2 J cm^{-2} , a frequency of 10 Hz, and
223 using a spot size of $110 \mu\text{m}$. Oxide levels were kept to a minimum (below 1%) and were
224 monitored using the ThO/Th ratio.

225 The reference glasses BHVO2-G and BCR2-G from the USGS and an in-house standard
226 SCO-1 (San Carlos olivine) were included during analytical runs to minimize matrix effects
227 (e.g., Bussweiler et al. 2019), and our measurements are within errors of the published values
228 for these international reference materials (see Table S4, e.g., Jochum et al. 2005; Bussweiler
229 et al. 2019). Elemental concentrations were calibrated against the glass standard NIST612 using
230 the values compiled by Jochum et al. (2005). Data were subsequently reduced using the
231 GLITTER software (Griffin et al. 2008) by carefully inspecting the time-resolved analyses to
232 exclude heterogeneity in the analyzed volume. Silica content (SiO_2 wt.% as determined by
233 μXRF) was used as an internal standard for both reference materials and olivine samples.

234 Local backgrounds were used instead of the interpolated or averaged session
235 background. This yielded variable detection limits for the various analyses, which were
236 occasionally either lower or higher than the typical detection limit; the best, worst, and typical
237 detection limits are provided in Table S4 while standard deviations are given together with the
238 LA-ICP-MS data. Reported trace and ultra-trace elemental concentrations in olivine correspond
239 to averages of at least four ablations per olivine grain. All elements were measured in a single
240 acquisition. Due to the formation of polyatomic interferences during LA-ICP-MS analysis,
241 several isotopes were measured for key elements. Olivine matrices are rich in Mg and the
242 formation of $^{25}\text{Mg}^{40}\text{Ar}$ overlaps with ^{65}Cu . Therefore, ^{63}Cu was used instead, given that ^{23}Na
243 in olivine is only a trace element. Furthermore, the excess on mass 65 is used to correct the
244 other Mg-argides on mass 64 and 66 corresponding to Zn. Similarly, the effect of oxide
245 formation on ^{45}Sc ($^{16}\text{O}^{29}\text{Si}$, natural ^{29}Si abundance is ca 4.68%) is corrected by deconvolving
246 the $^{44}\text{M}/^{43}\text{M}$ ratio ($^{44}\text{M}/^{43}\text{M}=(^{44}\text{Ca}+^{16}\text{O}^{28}\text{Si})/^{43}\text{Ca}$, ^{27}Al is a trace element in olivine and thus is
247 neglected, ^{28}Si natural abundance is ca. 92.23%) and subtracting the weighed excess from ^{45}M .
248 The accuracy of these corrections is ultimately assessed against certified reference glasses (e.g.

249 BHVO2-G and BCR2-G) and the in-house SCO-1 olivine standard. The measured isotopes
250 selected for this study are given in Table S4.

251

252 **3. Results**

253

254 We first present concentration and distribution of the major and minor elements, then
255 hydrogen concentrations followed by the other trace and finally ultra-traces elements. The same
256 color code is used throughout the set of figures and indicates the petrogenetic origin of the
257 olivine specimens: hydrogen-rich hydrothermal olivine (SAP, NW1, NW2) in dark-blue; the
258 hydrogen-poor hydrothermal olivine (MYA) in pale-blue; the magmatic olivine (LR) in black;
259 dark-green for the garnet-bearing peridotitic olivine (PA3); high temperature spinel-bearing
260 peridotitic olivine (SAS21) in brown-green, and at last the spinel-bearing peridotitic olivines
261 (DMP2, DMP4, SC, SC2018, SAS41, SAS20, OLM, PP, HS1, LAZ) in bright green.

262

263 *3.1 Major and minor element concentrations from X-ray fluorescence*

264

265 Olivine major and a few minor element concentrations determined by μ XRF are
266 reported in Table 2. FeO contents range from 5.77 to a maximum 15.58 wt.% FeO in the
267 magmatic olivine LR. Fo% ($= 100 \times (\text{Mg}/\text{Mg}+\text{Fe})$ a.p.f.u.) range from 83.2 (LR) to 94.1%
268 (MYA) as displayed in Figure 1. Nickel (0.23–0.47 wt.% NiO) and manganese contents (0.09–
269 0.18 wt.% MnO) are typical for olivine. An additional compilation of typical Fo% vs NiO
270 values are reported in Figure S5. Calcium concentrations range from 0.02 to 0.24 wt.% CaO.

271 NaO, TiO₂, Al₂O₃, and Cr₂O₃ contents are low, and fall mostly below the detection
272 limits of the μ XRF. Yet, μ XRF permits rapid determination of potential spatial heterogeneous

273 major element concentrations before FTIR and LA-ICP-MS analyses. We did not observe any
274 major or minor edge-to-edge zonings or micro-mineral inclusions or abnormal composition
275 areas in the μ XRF maps of the studied prisms of olivines.

276

277 *3.2 FTIR spectra and hydrogen concentrations*

278

279 Unpolarized spectra obtained on crystallographically unoriented olivines are shown in
280 Figure 2. Additional polarized spectra acquired on the crystallographically oriented olivine PA3
281 are shown in Figure 3. The entire set of unpolarized and polarized FTIR spectra are given in
282 Figure S2. The FTIR spectra display several OH bands of various intensities for only 11 of the
283 17 olivines analyzed; samples from San Carlos (SC and SC2018), Damaping (DMP2 and
284 DMP4), and two of the gem olivines (HS and PP) are hydrogen-free. The wavenumbers of the
285 OH bands are reported for each sample in Table 1 and as previously reported for iron-bearing
286 olivines, for two ranges of wavenumbers (e.g., Miller et al. 1987; Kohlstedt et al. 1996; Göse
287 et al. 2010; Demouchy and Bolfan-Casanova 2016; Thoraval et al. 2019). Range 1 includes
288 wavenumbers between 3650 and 3500 cm^{-1} and Range 2 from 3500 to 3000 cm^{-1} . The polarized
289 FTIR spectra of PA3 shown in Figure 3 are typical of garnet-bearing mantle peridotites (e.g.,
290 Miller et al., 1987).

291 Hydrogen concentrations derived from FTIR spectra are reported in Table 3. We report
292 hydrogen concentrations determined using the calibration of Paterson (1982) for unpolarized
293 IR spectra and using the more recent mineral-dependent calibration of Withers et al. (2012) for
294 polarized IR spectra acquired along three orthogonal directions of the olivine prisms. The later
295 discussion refers only to hydrogen concentrations obtained using polarized spectra and the
296 calibration of Withers et al. (2012) ('[OH] po W' in Table 3). Hydrogen concentrations in
297 hydrogen-bearing olivines range from 4 (LAZ) to 54 ppm H_2O wt (NW1), spanning a large

298 range of concentrations typical of olivines in off-craton settings (e.g., Ingrin and Skogby 2000;
299 Peslier 2010; Demouchy and Bolfan-Casanova 2016). We also measured profiles, and they did
300 not reveal special heterogeneous concentrations expect for PA3 (e.g., Figure S3), with very
301 limited edge depletion after removal of the original grain rim as illustrated in Figure 4. This
302 agrees with previous reports for olivine from this locality (Demouchy 2004; Demouchy et al.
303 2006).

304 Overall, and despite significant scatter, mantle olivines constitute a broad positive array
305 of hydrogen concentrations as a function of Fo% shown in Figure 5. Hydrothermal MYA, NW1,
306 and NW2 olivines have the highest Fo% (>93.6) but MYA has low hydrogen concentration (~6
307 ppm H₂O wt, respectively) despite its high Fo%. The high hydrogen concentrations observed
308 at high Fo% contrast strongly with the H-free to low hydrogen concentrations (<10 ppm H₂O
309 wt) of the low-Fo% (<90), which can be called “fertile” olivines (Fig. 5).

310

311 *3.3 Minor, trace, and ultra-trace element concentrations*

312

313 As the aim of this study is the decipher atomic impurities as extrinsic defect populations,
314 we have chosen to sort and group the elements first by concentration level, and second by
315 cationic valences.

316

317 LA-ICP-MS analyses permit the quantification of a large range of minor, trace, and
318 ultra-trace element concentrations, reported in Table 4 (see Table S4 for detection limits), which
319 vary enormously between 3306 ppm Ni (LAZ) down to 0.04 – 0.05 ppb (e.g., Tb in MYA or
320 Th in DMP4, this is equivalent to $4 - 5 \times 10^{-11} \text{ g g}^{-1}$). Here we have considered that a *minor*
321 *element* has a concentration above 1000 ppm, *trace elements* between 1000 and 10 ppm, and
322 we introduce the *low trace elements* with concentrations between 10 and 0.1 ppm (i.e., two

323 orders of magnitude for each group) and finally below 0.1 ppm for the *ultra-trace elements*.
324 Several elements have very variable concentrations in olivine (e.g., Al, between 0.9 and 224
325 ppm, Cu between 0.005 and 4.24 ppm), in agreement with the different petrogeneses.
326 Furthermore, we have summarized in Table S5 the sorting and ranking of the element as a
327 function of their abundance level, which is later used for the sum of concentrations displayed
328 in Figure 6. The rare earth elements (REEs) in olivine all show concentrations below 0.1 ppm
329 and are therefore here referred to as ultra-trace elements.

330

331 *3.3.1 Minor elements*

332

333 The only elements present at minor levels within the entire olivine set are Ni and Mn,
334 their sum ranges from 3071 (NW1 and NW2) to 4333 ppm LAZ (Table 4). One sample has also
335 a high Ca concentration (1437 ppm Ca in LR olivine). The sums of minor elements are inversely
336 correlated with hydrogen concentrations (Figure 6a). Ni dominates the sum of the minor
337 elements in each sample, followed by Mn (706 – 1390 ppm) and to some extent Ca (31 – 1437
338 ppm). Three olivines (NW1, NW2, and SAP) have high B concentrations with values between
339 61 and 110 ppm (Table 4), thus significantly higher than the relatively constant B
340 concentrations of the other olivines (1.58 ± 0.50 ppm), but not reaching a minor element
341 concentration level. These three relatively B-rich hydrothermal olivines are characterized by
342 lower Ni (1697 – 2676 ppm) and Ca concentrations (30 – 40 ppm) than other olivines and have
343 extremely low Al concentrations (<1 ppm).

344 The different petrological groups (color coded) are well recognized in Figure 6, but we
345 can further define groups I, II, and III, notably in Figure 6b (i.e., area surrounded by the grey
346 dashed lines). Group-I includes hydrogen-rich hydrothermal olivines (NW1, NW2, and SAP),
347 and poor in minor elements. Group-II comprises the minor-element-rich olivines with moderate

348 to high H contents (PA3, SAS20, SAS21, and LR). Finally, group-III with the H-poor to H-free
349 olivines (DMP, OLM, LAZ, SC, and the H-poor hydrothermal olivine MYA).

350

351 *3.3.2 Trace, low-trace and ultra-trace elements*

352 LA-ICP-MS analyses yield elements at low (ppm level) to very low concentrations (ppb
353 level) in olivine (Table 4). The total combined concentration of trace, low trace and ultra-trace
354 impurities as a function of hydrogen concentration per sample ranges from 312 to 1496 ppm
355 (presented by level of concentration in Fig. 6b, c and d). There is an inverse relationship
356 between the sum of trace element and H concentration in olivine as illustrated in Fig. 6b, within
357 each group.

358 One can notice graphically that groups-I and II are in prolongation of each other and
359 that group III is shifted down in H concentration compared to groups I and II. The low-H
360 hydrothermal olivine (MYA) also aligns with the sp-lherzolite olivine of group III. The olivine
361 most enriched in trace elements is magmatic olivine LR (Table 4), and those with the lowest
362 trace element contents are the hydrothermal samples (SAP, NW1, NW2, MYA). The groups I,
363 II and III are further confirmed by trace to trace element concentrations (H excluded, B versus
364 Li, Cr versus B; Ti versus Cr/Na; Ti versus V; Cr versus V, Cr versus Al, Li versus P) as
365 illustrated in Figures S6 and S7.

366 The total concentration of ultra-trace impurities per sample ranges from 0.07 to 0.45
367 ppm (Table 4) and are shown in Figure 6d. While we previously identified three groups (I, II,
368 and III), the REE concentrations for all samples are extremely low and the distribution
369 according to those groups is not as clear as in Fig. 6b; the sum of REE contents per sample
370 varies between 4 and 140 ppb (Table 4). However, if the four hydrothermal B-rich olivines and
371 the magmatic olivine LR are discarded, this range is reduced to 4 - 31 ppb. Although MYA
372 (highest Fo% = 94.11) shows the lowest REE content and $(Yb)_{PM}$ value (here, the subscript

373 'PM' indicating normalization to the primitive mantle value; McDonough and Sun, 1995).
374 Overall, the summed REE concentrations in the olivines appear uncorrelated to Fo% and other
375 divalent impurities.

376 REE patterns and Th concentrations are reported normalized to primitive mantle values
377 (McDonough and Sun, 1995) in Figure 7. Except for four samples, the olivine REE patterns are
378 broadly similar. These four exceptions are the three H-rich hydrothermal olivines (NW1, NW2,
379 SAP) and the magmatic olivine LR. These peculiar olivines are characterized by much higher
380 heavy-REE contents ($(Yb)_{PM} = 0.16$ for SAP) than the other olivines (e.g., $(Yb)_{PM} = 0.011$ for
381 SC2018). Furthermore, the REE patterns of SAP and LAZ are similar in shape, i.e., less
382 depleted in light-REEs ($Ce/Yb = 0.778$ for LAZ) than the other olivines (on average, $Ce/Yb =$
383 0.085 ± 0.090). The remaining olivines have REE patterns characterized by a steady, negatively
384 sloped heavy-REEs to middle REE patterns ($(Yb/Gd)_{PM} = 0.81$) and enrichments of Th and La
385 relative to Ce ($(La/Ce)_{PM} = 0.387$ for SC2018). Large ion lithophile elements (LILEs: Sr, Rb,
386 Ba, U), Ce, and Th show relatively similar patterns and abundances in all olivines, including
387 the four anomalous specimens mentioned above. For instance, U contents are relatively high
388 ($(U/Th)_{PM} > 1$), whereas Rb is systematically enriched relative to Ba ($(Rb/Ba) > 1.4$ for SAS20).
389 All olivines show negative Sr anomalies relative to Pr or Nd. The behavior of high field strength
390 elements (HFSEs: Ti, Zr, Hf, Nb, Ta) relative to the REEs is much more variable. Overall,
391 HFSEs do not form negative anomalies relative to their neighboring REEs, except occasionally
392 for Zr, and either follow the continuity of the REE pattern or produce marked positive
393 anomalies. Although REEs occur in very low concentrations in olivine, hydrogen is not as
394 depleted as La and Ce. Also seen in Figure 7, the ultra-trace element patterns of mantle-derived
395 olivines (i.e., excluding those of hydrothermal and magmatic origins) are quite similar among
396 the analyzed specimens, and are mostly irrespective of petrological contexts (e.g., melting and
397 metasomatic indexes). The relative consistency of ultra-trace element concentrations and

398 fractionations in olivine, whatever the geological setting and trace element concentration of the
399 coexisting phases (e.g., pyroxenes), have been previously observed by Bedini and Bodinier
400 (1999) and Garrido et al. (2000). Our results further confirm that the incorporation of these
401 elements (REEs, HFSEs, \pm LILEs) into mantle olivine is governed by olivine crystallography.
402 Thus, incorporation is limited by vacancy population and concentrations, and not by the
403 chemical compositions of coexisting phases or past percolating melts and fluids.

404

405 *3.4 Distribution by valence and relationship with H*

406

407 Point defect theory accounts for mass conservation, the respect of crystallography (i.e.,
408 site balance) and electroneutrality (i.e., charge balance) to minimize defect energy. Therefore,
409 atomic impurities are ‘aware’ of each other and should further be decrypted as a function of
410 their valence. In the past, mechanisms of hydrogen incorporation were successfully decrypted
411 as a function of the occupied vacancies (V), which is limited to V_{Si}'''' and V_{Mg}'' (using Kröger-
412 Vink notation, Kröger and Vink, 1956), and to possible mere interstitial proton (h_i). In
413 addition, two mechanisms of coupled (or associated) point defect were identified between
414 trivalent and hydrogen (e.g., Fe^{3+} , Cr^{3+} , Mackwell and Kohlstedt 1990; Tollan et al. 2018) and
415 between titanium and hydrogen (the so call Ti-clinohumite-like point defect, e.g., Berry et al.
416 2005). The established hydrogenated point defect and their matching IR bands are already given
417 in Table 1. Occupancies of H in V_{Si}'''' is attributed to IR bands at 3598, 3562, 3542, and 3485
418 cm^{-1} , without information on the number of H inside the tetrahedron. Occupancies of H in V_{Mg}''
419 is attributed to 3230 cm^{-1} , again without information on the number of H inside the octahedron
420 (e.g., Berry et al., 2007). Hydrogen coupled to trivalent impurities yields IR bands at 3355 and
421 3327 cm^{-1} (e.g., Berry et al. 2007, Blanchard et al. 2017; Tollan et al. 2018). At last, hydrogen
422 in V_{Si}'''' balanced by Ti in V_{Mg}'' yields IR bands at 3572 and 3525 cm^{-1} . Therefore, hydrogen

423 mechanisms of incorporation can be inferred by ‘reading’ an infrared spectrum with this
424 framework of four mechanisms. Nevertheless, in the experimental studies, hydrogenation under
425 water saturation was preceded by doping of the olivine lattice with large amount of one type of
426 atomic impurity (Berry et al. 2005, 2007, Padrón-Navarta et al. 2014) and for a given restricted
427 set of thermodynamic conditions (fO_2 , fH_2O , $aSiO_2$), which is not necessarily relevant for the
428 entire upper mantle but for a specific context only (e.g., for subduction, Padrón-Navarta and
429 Hermann, 2017).

430 Below we report the distribution of hydrogen as a function of the valence of co-existing
431 impurities for concentration levels found in natural olivine specimens. From now on, element
432 concentrations are presented in molar concentration (in micromol/g) to better assess associated
433 point defects. The sum of monovalent, divalent, trivalent, tetravalent and pentavalent as a
434 function of hydrogen concentration in ppm of hydrogen by weight are also provided in Figure
435 S8.

436 Monovalent distribution is dominated by Li and Na, they are presented individually and
437 as a sum in Figure 8. No major Li variation as a function of hydrogen is observed in most of
438 the olivines, except for the hydrogen-rich hydrothermal samples (NW1 or NW2), which display
439 high Li and low Na concentrations. In the contrary, Na distribution is more variable from very
440 poor (0.08 ppm Na in NW2) to high (58.1 ppm Na in LR and 63.7 ppm Na in PA3).

441 Divalent distribution is dominated by Ni, Mn, Ca and was already identified in Figure
442 6a and 6b. Since the concentration level of Ni is very high compared to other divalent
443 impurities, the negative correlation observed on Figure 6a is not perturbed by the addition of
444 other metal-like divalent impurities. However, if nickel is excluded, the sum of divalent
445 elements is not strikingly negatively correlated (Fig. S8).

446 The sum of trace trivalent distribution (B, Al, Cr, Sc and V) is very different if we
447 compare the hydrothermal olivines from the others olivines as shown in Figure 9. The mantle

448 olivines and LR olivine are presented together in Figure 9a and b and the hydrothermal olivines
449 in Figure 9c. If the IR bands attributed to hydrogen - trivalent complex defects (3355 and 3327
450 cm^{-1}) are only considered, the mantle-derived olivines display a positive correlation ($R^2 = 0.83$).
451 A similar distribution is observed for most of the trivalent impurities, including the sum of
452 REEs as shown in Figure 9b. Note that B (1.16 – 2.18 ppm or 0.11 – 0.2 micromol/g) and Sc
453 (5.83 – 9.5 ppm or 0.13 – 0.21 micromol/g) do not show such a clear relationship, as they have
454 a limited range of concentrations when compared to other trivalent elements (one or more order
455 of magnitude for Cr, Al and V). The magmatic olivine (LR) is singled out by its high
456 concentration in trivalent elements, which was also observed for the other atomic impurities.

457 The sum of the concentration of main trivalent elements (B+Al+Sc+Cr+V) as a function
458 of bulk hydrogen concentration for the hydrothermal olivines is shown in Figure 9c and displays
459 positive correlation ($R^2 = 0.98$), which is also visible if only B is considered, even if the
460 correlation is not as good as for the sum of trivalent elements. For the hydrothermal olivines,
461 the mechanism of coupling is likely to involve B siting into V_{Si}'''' and two H in V_{Mg}'' as
462 previously suggested by Sykes and Rossmann (1994) to lead to $\{2H_{Mg}^{\times}B'_{Si}O_{O}^{\times}\}'$ complex
463 defect, but which is not electronically balanced. It can also lead to a simplified defect suggested
464 by e.g., Christ (1965) with $\{2Mg_{Mg}^{\times}B'_{Si}(OH)_{O}\}^{\times}$ even if the complete substitution (for every Si
465 atomic) is not realistic in these olivines. Unfortunately, our hydrothermal olivines do not permit
466 to make a distinction between these two different complex point defects.

467 Lastly, the quantification of Fe^{3+} in olivine remains a true challenge (below Mössbauer
468 spectroscopy detection limits, e.g., 100 ppm e.g., Duba et al. 1973), and we could regrettably
469 not discuss the distribution of Fe^{3+} as a function of hydrogen in this study.

470 Tetravalent impurities, and in particular Ti, were the subject of specific attention as Ti
471 is responsible for the striking high intensity bands at 3575 and 3525 cm^{-1} (e.g., Berry et al.
472 2005), in a majority of mantle-derived olivines (Fig. 2). The titanium clinohumite-like point

473 defect is defined as a Ti^{4+} ion occupying a Mg vacancy and two H^+ ions occupying a Si vacancy
474 (Berry et al. 2005, 2007b; Walker et al. 2007; Padrón-Navarta et al. 2014; Padrón-Navarta and
475 Hermann 2017). It is noted $\{Ti_{Mg}^{2+}(2H)_{Si}^{2-}O_O^{\times}\}^{\times}$ in Kröger-Vink notation or abbreviated as [Ti-
476 2H]. Nevertheless, for our data set there is no striking positive correlation between the bulk
477 mineral hydrogen concentration and Ti concentrations in the studied olivines (Fig. S8). Only
478 six of the analyzed olivine samples (OLM, SAS20, SAS41, Pa3, LR and LAZ, see Table 1)
479 displayed the typical OH bands attributed to the [Ti-2H] defect (3575 and 3525 cm^{-1}). However,
480 if we only consider the hydrogen associated with these IR bands, a slightly positive correlation
481 is seen in Figure 10a ($R^2=0.65$) (i.e., deconvolution results are given in Fig. S4; integrated
482 normalized absorptions and % relative to bulk hydrogen concentrations are detailed in Table
483 S2). We added in Figure 10b typical Ti range of concentrations reported in mantle-derived
484 olivines (see also Fig. 2 in Foley et al., 2013). We compare our results with FTIR results from
485 doping experiments (Faul et al. 2016; Padrón-Navarta and Hermann 2017, Tollan et al. 2018)
486 and from mantle-derived olivines (Schmaedicke et al. 2013; Demouchy et al. 2015; Denis et al.
487 2018), which were all reprocessed accordingly to the methodology used here to obtain the
488 normalized integrated absorbance for the [Ti-2H] defect only. We converted the concentration
489 in micromole/g to better evaluate the potential coupling between hydrogen and titanium in
490 Figure 10c. The results are far from the expected 1:2 line (at saturation), but closer to a 1:1
491 coupling. Note that error bars from Padrón-Navarta et al. (2014) are very large since titanium
492 concentrations were obtained by electron microprobe and not LA-ICP-MS; We also wish to
493 point out the non-negligible impact of the choice of the IR calibration (Bell et al. 2003 versus
494 Withers et al. 2012) as illustrated by Figure 10c. We reiterate that such a positive correlation
495 does not hold when considering the bulk (total) hydrogen contents. This discrepancy shows that
496 even if the [Ti-2H] defect is a significant mechanism for hydrogen incorporation in mantle
497 olivine, it is not dominant enough to overcome the other mechanisms (see Table S2). We thus

498 conclude that the diversity of hydrogen-decorated point defects dilutes the effect of complex
499 defect with Ti.

500 To assess how our olivines match current Ti data, we further compare our results with
501 mantle and magmatic compositions from the literature for Ti and Ca in Figure 11 as these trace
502 elements are commonly used together as a petrogenetic indicator (e.g., O'Reilly et al., 1997;
503 Foley et al., 2013). This figure demonstrates that mantle-derived olivines have low Ti (<100
504 ppm) and Ca concentrations (<1000 ppm). Conversely, Ti- and Ca-rich compositions are typical
505 of magmatic olivines (e.g., sample LR). Hence, Figure 11 provides a framework for further
506 doping experiments to properly assess the potential impact of non-divalent minor elements such
507 as Ti when co-existing with various divalent cations (e.g., Ni, Ca, Mn) in lithospheric olivines.

508 The most abundant pentavalent impurity (phosphorous, Fig. S8d) has a similar
509 concentration level to monovalent and titanium, but a distribution similar to trivalent elements,
510 except for the high temperature (HT) harzburgitic olivine, which is one of the poorest olivine
511 in P.

512

513 **4. Discussion**

514

515 *4.1 Potential impact of hydrogen loss*

516

517 Only one of the selected olivine samples originally displays a heterogeneous hydrogen
518 distribution (PA3, Fig. 4), which was interpreted as resulting from partial dehydration by
519 diffusion during magma ascent towards the surface (Demouchy et al. 2006). Other studies have
520 reported similar dehydration profiles in olivines and pyroxenes (Peslier and Luhr 2006; Wade
521 et al. 2008; Lloyd et al. 2012, 2017; Denis et al. 2013; Peslier et al. 2015; Tian et al. 2017;
522 Denis et al. 2018). However, after more than a decade, we must face the paucity of olivines and

523 pyroxenes presenting such heterogeneous hydrogen distributions, which are also never coupled
524 with other minor/trace element spatial heterogeneities. Furthermore, despite the fast hydrogen
525 diffusivities obtained experimentally (Mackwell and Kohlstedt 1990; Demouchy and Mackwell
526 2006), natural olivine crystals ubiquitously contain remnant traces of hydrogen. In this study,
527 we assume that the remnant hydrogen accurately represents the energetically favorable long-
528 term hydrogen-decorated point defects and their diversity. We emphasize that additional
529 hydrogen-decorated defects may be present in the olivine lattice at depth, but not preserved
530 during magma ascent (e.g., Kempf and Herrmann 2018; Tollan et al. 2018), hence we do not
531 consider them as reliable long-term mechanisms of hydrogen storage.

532

533 *4.2 Effects of temperature and pressure*

534 Because the incorporation of minor elements in mantle minerals is a function of
535 thermodynamic parameters (mostly temperature, pressure, and possibly oxygen fugacity)
536 several minor elements have been used as reliable geothermobarometers to estimate
537 equilibrium conditions in upper mantle rocks. For example, Ca exchange between ortho- and
538 clino-pyroxene or Ca in orthopyroxene (Ca-in-opx) is a function of temperature (e.g., Wells
539 1977; Boyd and Nixon 1978; Ellis and Green 1979; Brey and Kohler 1990) and aluminum
540 incorporation in olivine or pyroxene is a function of pressure (e.g., Stalder 2004; Férot and
541 Bolfan-Casanova 2012; Coogan et al. 2014; Bussweiler et al. 2017; D'Souza et al. 2020). In
542 particular, the Ca-in-opx geothermometer (Brey and Kohler 1990) has been widely used to
543 constrain the equilibrium temperature of mantle xenoliths (based on the fact that Ca
544 concentration increases in orthopyroxenes and decreases in olivine with increasing temperature;
545 e.g., O'Reilly et al. 1997), and to help constrain the pressure/depth of origin. Nevertheless, the
546 uncertainties on pressure remains most of the time very high for spinel-bearing peridotites (± 1
547 GPa and ± 100 °C; Brey and Kohler 1990). Nonetheless, in the absence of a better (absolute)

548 geothermobarometer, its usage quickly became the norm until recently (e.g., Wan et al. 2008;
549 Bussweiler et al. 2017; D'Souza et al. 2020). Combined with this geothermobarometer, the
550 maximum and minimum hydrogen concentrations in mantle-derived olivines display a striking
551 increase with increasing temperature as seen along a geotherm (Costa et al. 2010; Peslier et al.
552 2010; Demouchy and Bolfan-Casanova 2016; Peslier et al. 2017). This agrees with the
553 experimentally-determined control of water fugacity on hydrogen incorporation with increasing
554 pressure under water-saturation (Kohlstedt et al. 1996; Hirschmann et al. 2005; Mosenfelder et
555 al. 2006; Bali et al. 2008; Férot and Bolfan-Casanova 2012; Gaetani et al. 2014; Padrón-Navarta
556 and Hermann 2017). However, in naturally hydrated mantle olivines, this positive correlation
557 might not be that straightforward and could be indirect. Here, we examine the possible
558 correlation between hydrogen and Ca concentrations from this study and from mantle-derived
559 olivines in Figure 12 (Demouchy 2004; Mosenfelder et al. 2006; Grant et al. 2007; Falus et al.
560 2008; Li et al. 2008; Yang et al. 2008; Peslier et al. 2010, 2012; Denis et al. 2013, 2015, 2018;
561 Soustelle et al. 2013; Demouchy et al. 2015, 2019; Satsukawa et al. 2017). Hydrogen
562 concentration broadly increases with decreasing Ca concentration in olivine in group III
563 confirming that the two species compete for M-site vacancies with increasing temperature (or
564 depth). The three hydrothermal olivines of Group I do not show the same trend. The olivines
565 from Group II do not show a well-defined correlation as for group III, and the horizontal spread
566 is dragged by the composition of the magmatic olivine LR. We recall here that magmatic
567 olivines (e.g. LR) are highly defective as the Fe-enrichment, resulting from crystallization in a
568 Fe-rich magma, enhances nonstoichiometry (e.g, Nakamura and Schmalzried 1983), thus
569 vacancy concentration, and consequently incorporation of atomic impurities such as Ca is easier.
570 Nevertheless, if the magma is far to be water-undersaturated (e.g., water-fugacity is low at
571 shallow depth), it cannot lead to a concomitant high incorporation of hydrogen, thus hydrogen
572 will be at odd with the other atomic impurities in magmatic olivines. To resume, while

573 magmatic olivines will have a high capacity to host H, ultimately the concentration of H in
574 these same olivines will depend on the water fugacity in the magmatic system.

575

576 *4.3 Co-existence of complex hydrogenated point defects*

577 The identification of a dominant and unique mechanism of hydrogen incorporation in
578 olivine relevant to Earth's mantle conditions has been the subject of important consideration.
579 Early experimental studies established the important role of M-site vacancies in hydrogen
580 incorporation (Beran and Putnis 1983; Kohlstedt et al. 1996; Bali et al. 2008; Férot and Bolfan-
581 Casanova 2012; Gaetani et al. 2014). Experimental studies have now clearly documented
582 increased hydrogen incorporation in minor- and trace-element-doped crystals. Furthermore, the
583 strategic role of Ti and its association with H incorporation into Si vacancies (the titanium
584 clinohumite-like point defect) is now well established. Here, the Figures 2, 6a, 9, 10 and Table
585 S4 clearly show that the integrated OH bands for [Ti-2H] are the most intense OH bands in
586 FTIR spectra for mantle olivines. Despite this, integrated OH bands for [Ti-2H] do not
587 exclusively control the bulk H concentration and thus cannot be used a distinctive proxy for the
588 bulk hydrogen concentration in olivine for water under-saturated conditions compared to the
589 three other mechanisms of hydrogen incorporation ($V_{Si}^{''''}$, $V_{Mg}^{''}$ and coupling with trivalent
590 impurities). Nevertheless, the sum of the hydrogen concentration linked to the four mechanisms
591 of incorporation seem to hold true as shown in Figure 13. Indeed, excluding three olivines from
592 group II (magmatic LR, garnet-bearing lherzolite and the HT harzburgite), olivine forms a
593 linear positive correlation parallel to the 1:1 line. Furthermore, if we take into consideration the
594 entire population of atomic impurities in mole per gram of olivine the sum of trivalent
595 impurities (B+Al+Cr+Sc+V= 1.14 to 17.2 $\mu\text{mol/g}$) dominates the sum of monovalent
596 (H+Li+Na =1.07 to 6.86 $\mu\text{mol/g}$), which is above pentavalent (e.g., phosphorous, 0.35 to
597 2.31 $\mu\text{mol/g}$) and the most abundant tetravalents elements (Ti+Ge = 0.09 to 1.14) as shown

598 in Figure S9. Then, hydrogen would mostly likely form complex associate-defect with trivalent
599 in natural olivines.

600

601

602 **5. Conclusions**

603 The incorporation of minor, trace, and ultra-trace elements into atomic-scale defects has
604 been used as a petrogenetic indicator of magmatic and mantle processes (e.g., Foley et al. 2013).
605 Here, based on our study of olivine crystals from ten different geological localities, we draw
606 the following conclusions. (1) The diversity of hydrogen-decorated point defects is associated
607 with a large range of minor and trace elements. Nevertheless, no single impurity seems to
608 control the bulk incorporation of hydrogen in olivine. Furthermore, the effect of titanium
609 clinohumite-like point defects appears diluted once bulk hydrogen concentrations are
610 considered in mantle-derived olivines. (2) Incorporation of these elements (REEs, HFSEs, \pm
611 LILEs) into mantle olivine appears to be governed by olivine crystallography. This is limited
612 by vacancy population and concentrations for a given temperature, and not by the chemical
613 compositions of coexisting phases or percolating melts and fluids. (3) Although REEs occur in
614 very low concentrations in olivine, olivine is not as depleted in H as in La and Ce, probably due
615 to difference in their valence.

616 The geochemical affinity of hydrogen appears inconsistent, a peculiarity which is
617 probably related to its small ionic radius, the increasing vacancy population in olivine with
618 increasing temperature (and then depth), the diversity of complex defects, and the very fast
619 diffusivity of hydrogen in olivine relative to other minor/trace elements (e.g., fast to reach new
620 equilibrium). This observed behavior could be explained by a late incorporation of hydrogen
621 into olivine, with hydrogen filling all persisting vacancies in the olivine lattice (e.g., post-partial
622 melting, post-metasomatism). Thus, H is offered a large range of sites of storage, and can be

623 categorized as a versatile and opportunistic atom; H can be seen as a cuckoo element using
624 whatever atomic spaces which remain available.

625 As a consequence, targeting a single controlling mechanism of hydrogen incorporation
626 into olivine using natural specimens might be in vain. Solubility laws based on high-pressure
627 and high-temperature effects seem to remain the best approach, despite an inclination toward
628 over-doped and over-simplified incorporations of atomic impurities in experimental charges.
629 Furthermore, in ‘cold’ geological domains (e.g., subducted slabs, crustal and metamorphic
630 settings), the mechanisms of hydrogen incorporation might be overall different and more
631 complex than in mantle-derived contexts. This necessitates new and complex experimental
632 approaches to understand the role of co-existing atomic impurities in the mechanisms of
633 hydrogen incorporation and mobility in olivine as a function of the miscellaneous sites of
634 storage.

635

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646

647 **Availability of data and material**

648 All raw data are available upon request to the corresponding author.

649

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968

969 **Figure captions**

- 970 **Fig. 1** Forsterite contents ($Fo\% = 100 \times Mg/(Mg+Fe)$) of each analyzed olivine. Color coding:
971 Dark-blue for the hydrogen-rich hydrothermal olivine (SAP, NW1, NW2); pale-blue for
972 the hydrogen-poor hydrothermal olivine (MYA); black for the magmatic olivine (LR);
973 dark-green for the garnet-bearing peridotitic olivine (PA3); brown-green for high
974 temperature spinel-bearing peridotitic olivine (SAS21), and green for the spinel-bearing
975 peridotitic olivines (DMP2, DMP4, SC, SC2018, SAS41, SAS20, OLM, PP, HS1, LAZ).

976 **Fig. 2** Representative unpolarized infrared spectra for each olivine. All spectra are normalized
977 to 1 cm thickness, and off-set vertically for clarity. Polarized IR spectra triplets for each
978 sample are provided in Fig. S2. Color coding identical to Fig. 1 caption.

979 **Fig. 3** Representative polarized IR spectra for olivine PA3. All spectra are normalized to 1 cm
980 thickness, and off-set vertically for clarity.

981 **Fig. 4** Variations of the integrated absorbance (normalized to 1 cm of thickness and proportional
982 to hydrogen concentration) from polarized FTIR profiles of olivine PA3 along the
983 different crystallographic directions and for the three directions of polarization for the di-
984 electric vector.

985 **Fig. 5** Variations of hydrogen concentration as a function of forsterite content ($Fo\% = 100 \times$
986 $Mg/(Mg+Fe)$ a.p.f.u.). The primitive mantle value is ca. $Fo\% = 89.0$ (McDonough and
987 Sun, 1995). Color coding identical to Fig. 1 caption.

988 **Fig. 6** Variations of (a) hydrogen concentration in ppm H as a function of the sums of (a) minor,
989 elements, solid symbol Ni+Mn, hollow symbols Ni+Mn+Ca ; (b) Relationships between
990 the sum of trace elements contents and H concentration., with the three groups I, II, III,
991 (c) low trace elements and (d) ultra-trace element concentrations in ppm. Minor (ME),
992 Trace (TE), low -trace (LTE) and ultra-trace (UTE) elements are defined as follow: [ME]
993 ≥ 1000 ppm, $10 \leq [TE] < 1000$ ppm, $0.1 \leq [LTE] < 10$, $[UTE] < 0.1$ ppm, see text for further
994 detail and Table S5 for the listing of elements belonging to each set. Color coding
995 identical to Fig. 1 caption.

996 **Fig. 7** Selected trace and ultra-trace element concentration patterns normalized to the primitive
997 mantle composition (McDonough and Sun, 1995) for the studied olivines. For clarity, the
998 patterns are separated in two panels: (a) hydrothermal olivines (SAP, NW1, NW2, MYA)
999 and the magmatic olivine (LR). (b) all mantle derived olivines (OLM, SC, SC2018, PA3,
1000 SAS20, SAS21, SAS41, LAZ, HS1, PP, DMP2, DMP4). We added the in-house standard

1001 SCO1 as well. Note that the arrows are indicating that the concentrations for these
1002 elements are below detection limits (See Table S4 for detection limits).

1003 **Fig. 8** Variations of hydrogen concentrations as a function of monovalent elements: Li (cross
1004 symbol), Na (multiplication symbol) and both the sum of Li+Na (circle symbol). Color
1005 coding identical to Fig. 1 caption.

1006 **Fig. 9 (a)** Variations of hydrogen concentration linked to the 3355 and 3327 cm^{-1} IR bands as
1007 a function of the sums of trivalent element in all olivines. (b) Variations of hydrogen
1008 concentration as a function of Cr, Al, B, Sc, V and sum of REE in mantle-derived olivine
1009 and magmatic olivine displaying the 3355 and 3327 cm^{-1} IR bands. (c) Variations of bulk
1010 hydrogen concentration in the hydrothermal olivines (SAP, NMW1, NW2, MYA) as a
1011 function of the sum of trivalent elements (B+Al+Sc+Cr+V) and of B concentration (all
1012 in $\mu\text{mol}\cdot\text{g}^{-1}$). Color coding identical to Fig. 1 caption.

1013 **Fig. 10 (a)** Ti concentrations in ppm determined by LA-ICP-MS as a function of the normalized
1014 integrated absorbance from the two IR bands attributed to the titanium clinohumite-like
1015 point defects (3575 and 3525 cm^{-1}). Only samples displaying these OH bands are
1016 included here (see Table 1). For comparison, results from other studies are also reported
1017 (Demouchy et al., 2015; Faul et al., 2016; Padrón-Navarta and Hermann, 2017; Denis et
1018 al., 2018; Tollan et al., 2018). (b) Histogram of Ti concentrations observed in mantle-
1019 derived spinel-bearing and garnet-bearing peridotites (data from O'Reilly et al., 1997; De
1020 Hoog et al., 2010; Peslier, 2010; Peslier et al., 2012; Satsukawa et al., 2017). (c) Ti molar
1021 concentration as a function of H molar concentration in olivine from this study and from
1022 Padrón-Navarta and Hermann (2017) and Tollan et al., (2018) calculated from two
1023 different IR calibrations (B03: Bell et al., 2003) and W12 (Withers et al., 2012).

1024 **Fig. 11** Ti concentrations in ppm (logarithmic scale) as a function of Ca concentration in ppm
1025 in olivine from this study and from various lithology and/or geological settings:

1026 chondrules (Jacquet et al., 2012), megacrysts (Bell et al., 2004), kimberlites (Brett et al.,
1027 2009; De Hoog et al., 2010), picrites from Baffin (De Hoog, et al., 2010), lamprophyre
1028 (Prelevic and Foley, 2007; Foley et al., 2013), rift volcanics (Keller et al., 2006; Foley et
1029 al., 2013), metaserpentinites (De Hoog et al., 2014), and mantle xenoliths (O'Reilly et al.,
1030 1997; De Hoog et al., 2010; Peslier, 2010; Peslier et al., 2012; Satsukawa et al., 2017).

1031 **Fig. 12** Hydrogen concentrations as a function of Ca concentration in olivines from this study
1032 and from various studies on spinel-bearing and garnet-bearing mantle-derived peridotites
1033 (Demouchy, 2004; Grant et al., 2007; Falus et al., 2008; Li et al., 2008; Yang et al., 2008;
1034 Peslier et al., 2010, 2012; Denis et al., 2013, 2015, 2018; Soustelle et al., 2013; Demouchy
1035 et al., 2015, 2019; Satsukawa et al., 2017). Color coding identical to Fig. 1 caption.

1036 **Fig. 13** Variation of hydrogen molar concentrations against the sum of key atomic impurities
1037 all concentrations are in $\mu\text{mol}\cdot\text{g}^{-1}$. Key atomic impurities here presented are, (excluding
1038 divalent ions): solid symbols = the sum of the trace+low trace+ ultra-elements, and
1039 open symbols = the sum of Ti+B+Al+Cr+Sr+V. Color coding identical to Fig. 1
1040 caption.

1041

1042 **Table captions**

1043

1044 **Table 1** Olivine prism sizes after sample preparation and OH band positions for each olivine
1045 specimen as identified by unpolarized FTIR spectroscopy.

1046 **Table 2** Major and minor element concentrations determined by semi-quantitative μXRF for
1047 each olivine.

1048 **Table 3** Hydrogen concentrations (ppm H_2O wt) in olivine specimens obtained by unpolarized
1049 ('unpo') and polarized ('po') FTIR using the frequency-dependent calibration of Paterson
1050 (1982; 'Pat') and the mineral-dependent calibration of Withers et al. (2012; 'W')

1051 respectively. Concentrations are given in ppm H (equals to molar concentration), ppm of
1052 H₂O by weight and H/10⁶Si. The average integrated absorbances normalized to sample
1053 thickness are compiled in Table S1, and integrations were performed in the 3650–3050
1054 cm⁻¹ wavenumber range.

1055 **Table 4** Minor, trace, and ultra-trace element concentrations (ppm) measured by LA-ICP-MS
1056 analyses of the olivine specimens (*n* is the number of the measurements and ±1SD the
1057 standard deviation; typical detection limits for each element are given in Table S3).

1058

1059 **Supplementary material - Figure captions**

1060 **Fig. S1** (a) Photography of olivine specimens during cutting and polishing preparations step,
1061 from left to right, Norway, Sapat, San Carlos#1, #2, #3, La Réunion ; (b) Olivine
1062 specimens glue on glass section prior to X-ray fluorescence mapping and Laser ablation-
1063 inductively coupled plasma-mass spectrometry. One square is 5 mm.

1064 **Fig. S2** Sets of FTIR spectra of olivines not presented in the main text: (a) SAP, (b) MYA, (c)
1065 LR, (d) OLM, (e) NW1 and NW2, (f) SAS41, SAS20, and SAS21, (g) LAZ, (h) SC2018
1066 and SC, and (i) HS1, PP, and DMP. All spectra are normalized to 1 cm thickness.

1067 **Fig. S3** Integrated absorbance distributions across (a) SAS20 and (b) NW1 as representative of
1068 the homogeneous distributions observed across all olivine specimens except PA3

1069 **Fig. S4** Deconvolution details for the samples LR, LAZ, PA3, SAS20, SAS41, performed
1070 with the multipeak fitting package of IGOR PRO™
1071 (<https://www.wavemetrics.com/products/igorpro>)

1072 **Fig. S5** Variations of Ni content (at. ppm) as a function of forsterite content (Fo% = 100 ×
1073 Mg/(Mg+Fe) a.p.f.u.) in the olivines studied herein and in previous studies: garnet
1074 peridotites (Peslier et al., 2010, 2012), spinel-bearing peridotites (O'Reilly et al., 1997;
1075 Satsukawa et al., 2017), olivine phenocrysts from Aeolian island arc lavas (Zamboni et

1076 al., 2017; *NB*, the field of arc lavas extends down to 200 ppm Ni and Fo% = 60), olivine
1077 in various types of troctolites (Basch et al., 2018), and MORBs, OIBs (Hawaii), and
1078 Komatiites (Sobolev et al., 2007)

1079 **Fig. S6** Selected plots of trace elements as a function of trace element concentrations in $\mu\text{mol}\cdot\text{g}^{-1}$
1080 (B vs Li; Ti vs Cr/Na; Cr vs B; B vs H)

1081 **Fig. S7** Selected plots of trace elements as a function of trace element concentrations in
1082 $\mu\text{mol}\cdot\text{g}^{-1}$ (Ti vs V; Cr vs V; Cr vs Al; Li vs B)

1083 **Fig. S8** Sum of mono-, di-, tri-, tetra and penta-valent elements as a function of hydrogen
1084 concentration in ppm by weight.

1085 **Fig. S9.** (a) Sum of trivalent elements vs. sum of the monovalent elements; (b) Sum of trivalent
1086 elements vs. sum of the tetravalent elements; (c) Sum of tetravalent elements vs. sum of
1087 the monovalent elements; (d) Sum of pentavalent elements vs. sum of the monovalent
1088 elements.

1089

1090 **Supplementary material – Table captions**

1091

1092 **Table S1** Average integrated absorbances normalized to sample thickness in the studied
1093 olivines from unpolarized and polarized FTIR analyses in the 3650–3100 cm^{-1}
1094 wavenumber range

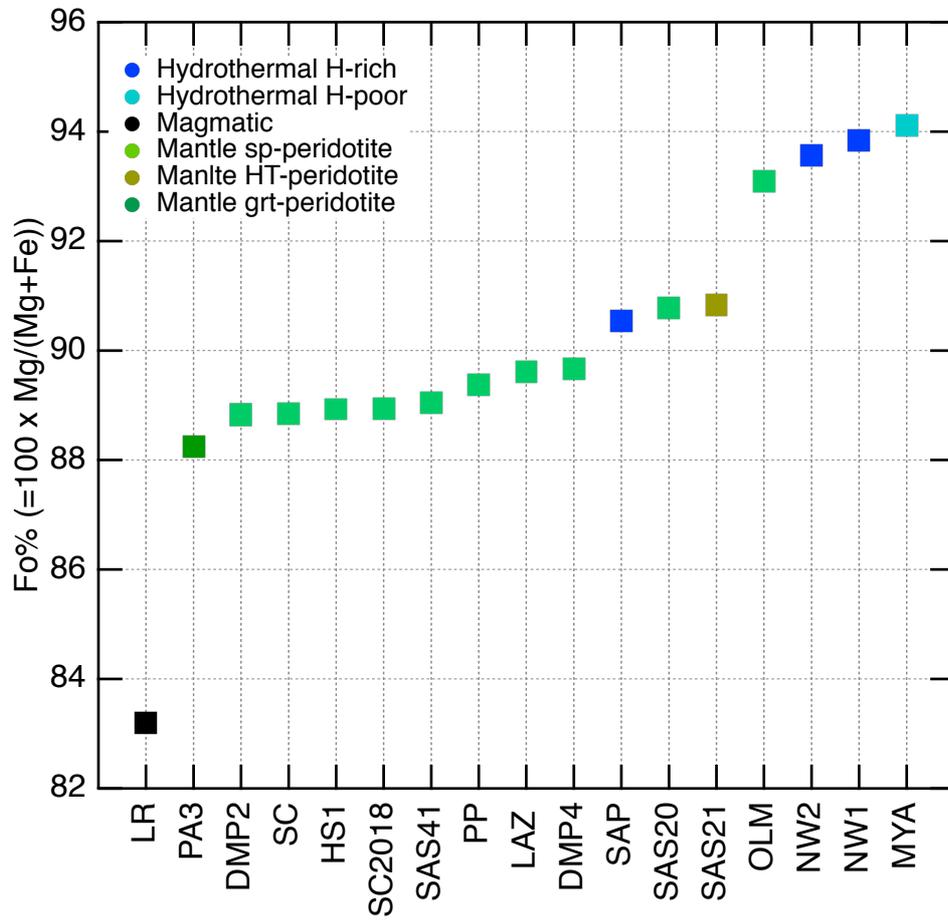
1095 **Table S2** Summary of the deconvolution results for unpolarized average spectra of olivines LR,
1096 LAZ, PA3, SAS20, SAS41, performed with the multipeak fitting package of IGOR PRO
1097 (<https://www.wavemetrics.com/products/igorpro>)

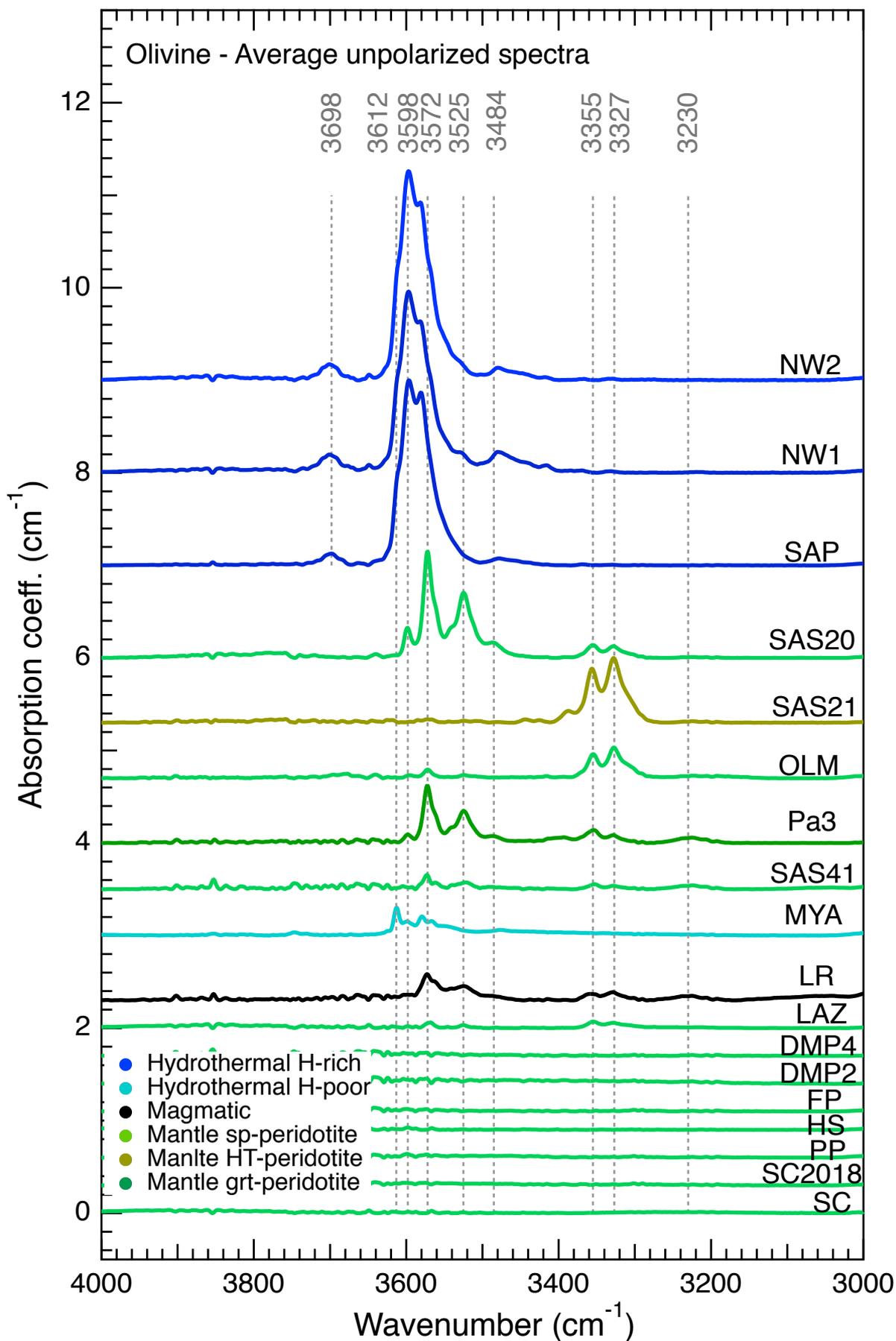
1098 **Table S3** Major and selected minor element concentrations for in-house standard SCO-1 as
1099 determined by μXRF , electron microprobe, and LA-ICP-MS analyses

1100 **Table S4** Minor, trace, and ultra-trace element concentrations determined by LA-ICP-MS for
1101 the standards used in this study (BCR2-G and BHVO2-G). Typical, best, and worst
1102 detection limits per element are also listed.

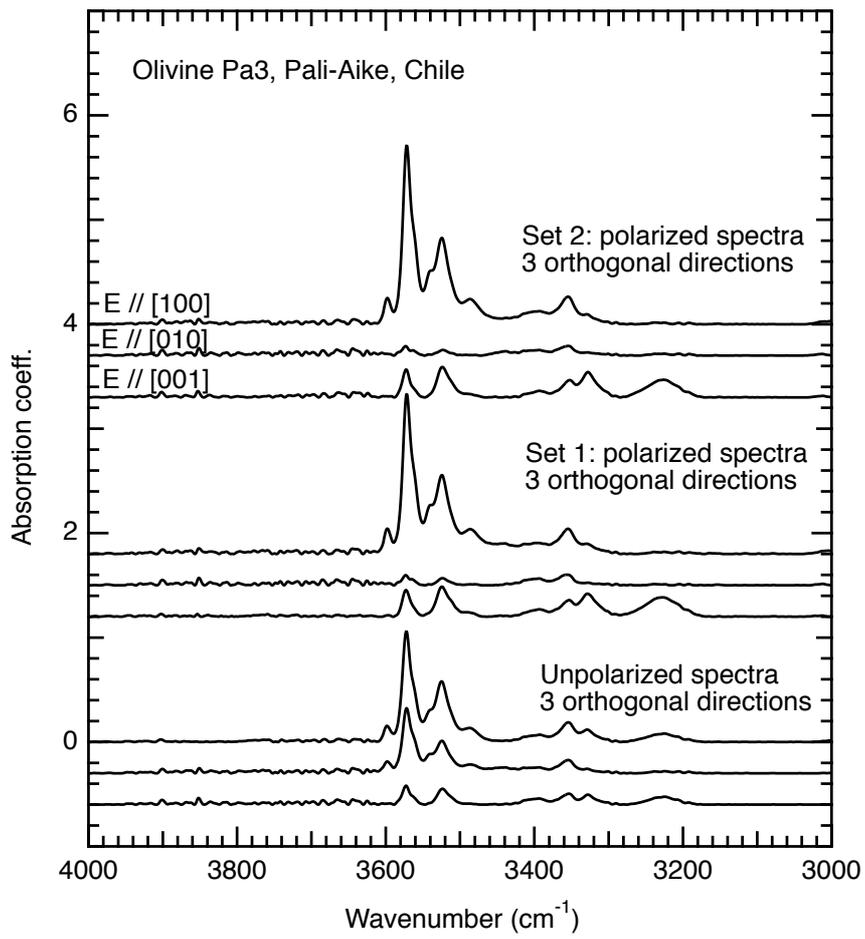
1103 **Table S5** Abundance and thus classification of the atomic impurities in each olivine used in the
1104 main text.

Demouchy and Alard, Fig. 1 Revised

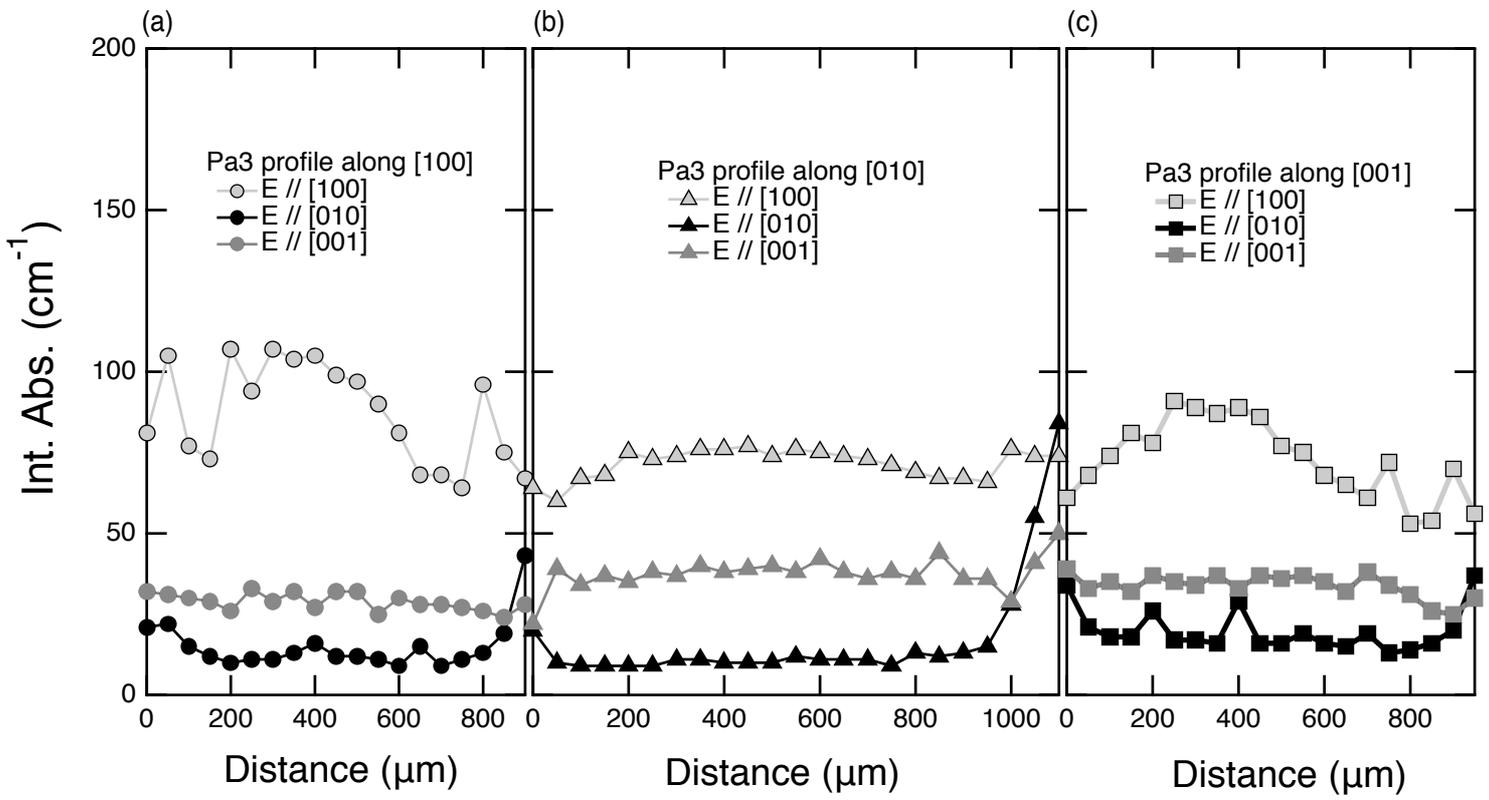




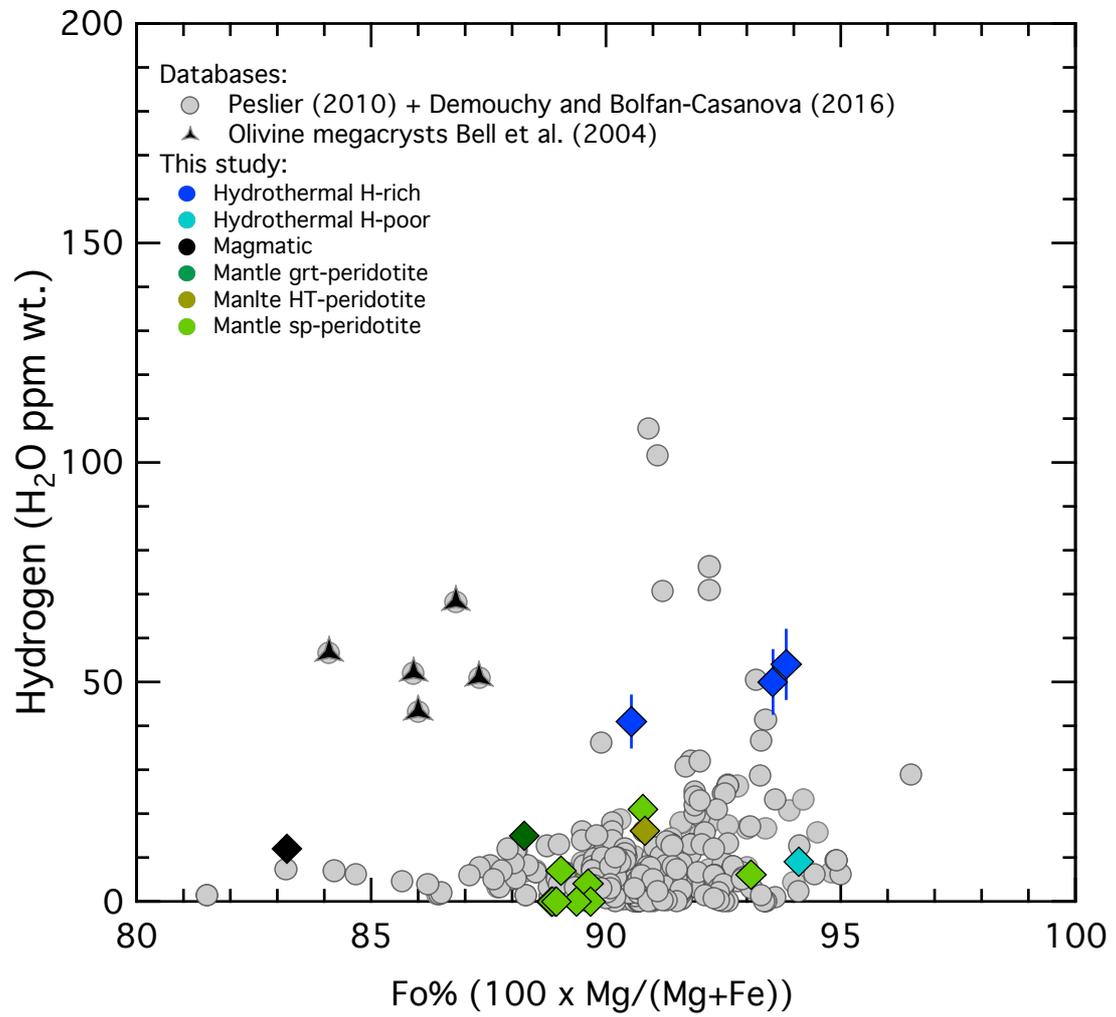
Demouchy and Alard, Fig. 3



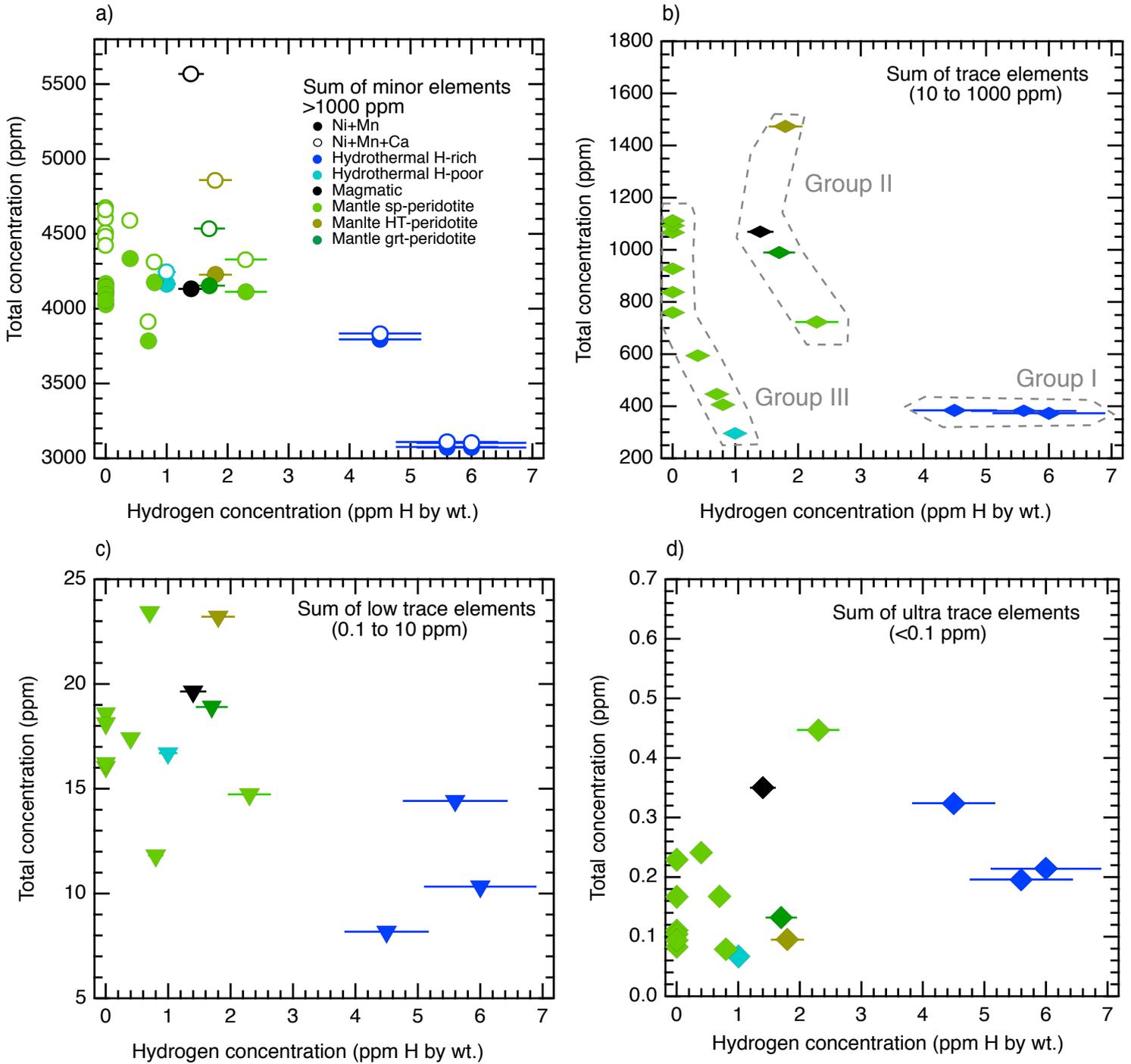
Demouchy and Alard, Fig. 4

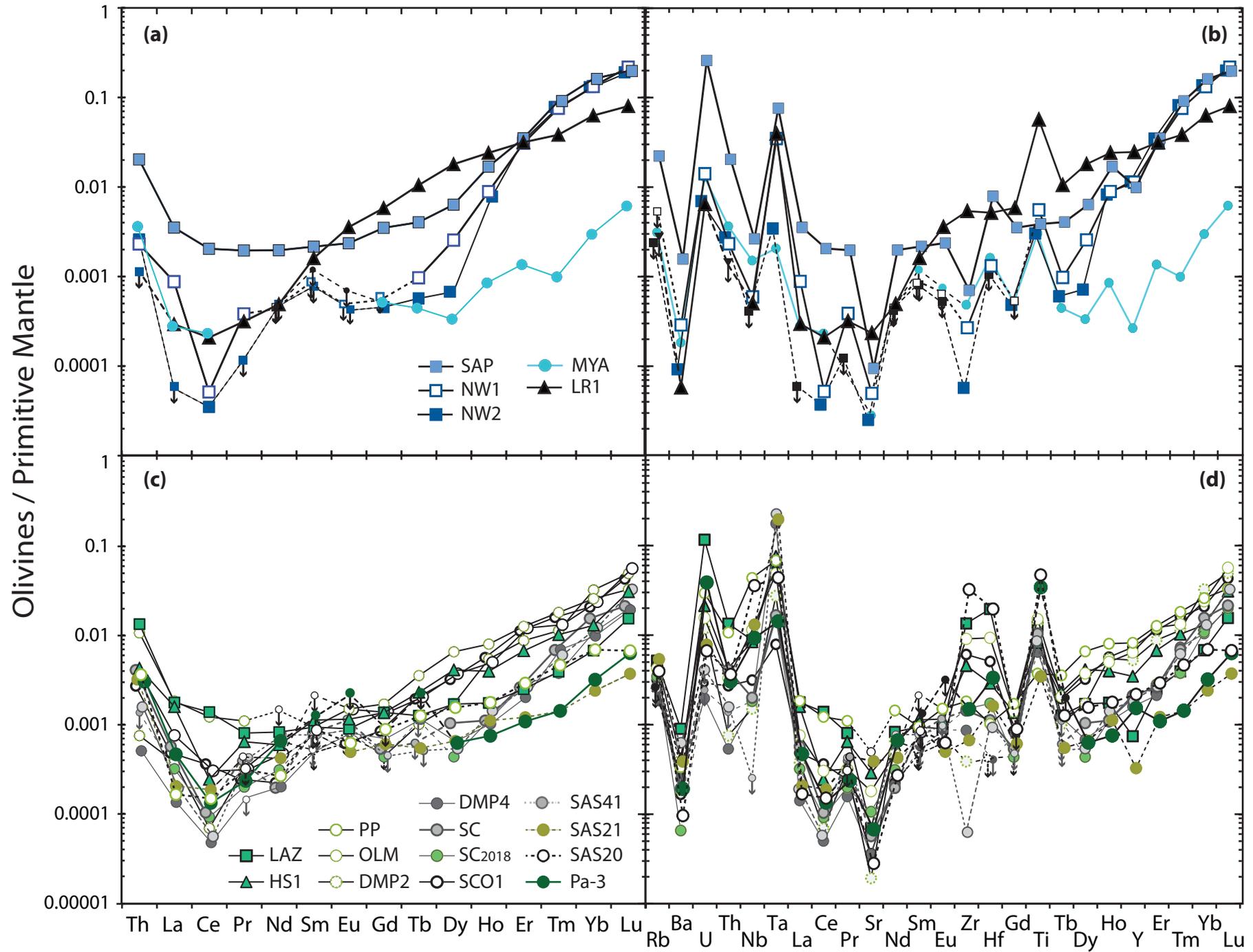


Demouchy and Alard, Fig. 5

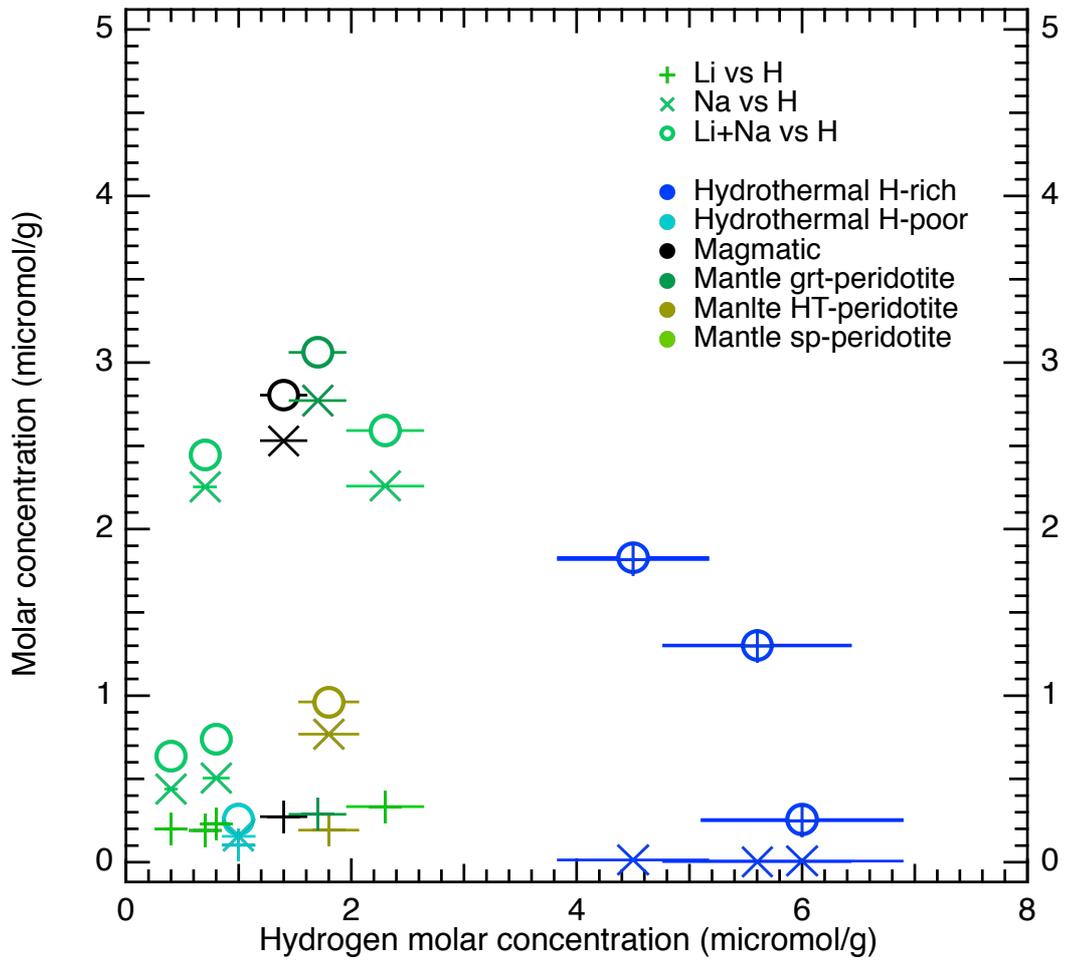


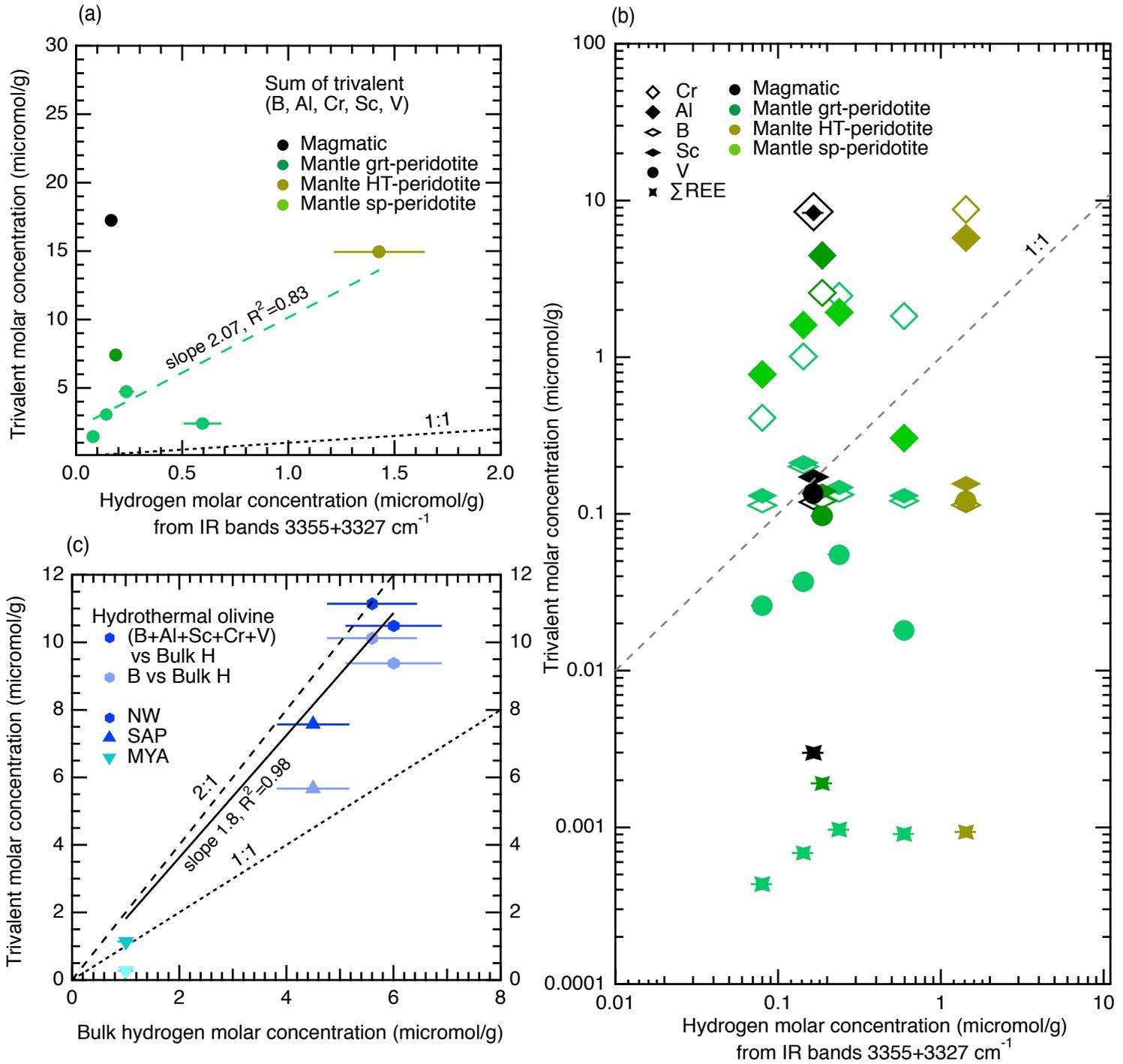
Demouchy and Alard, Fig. 6

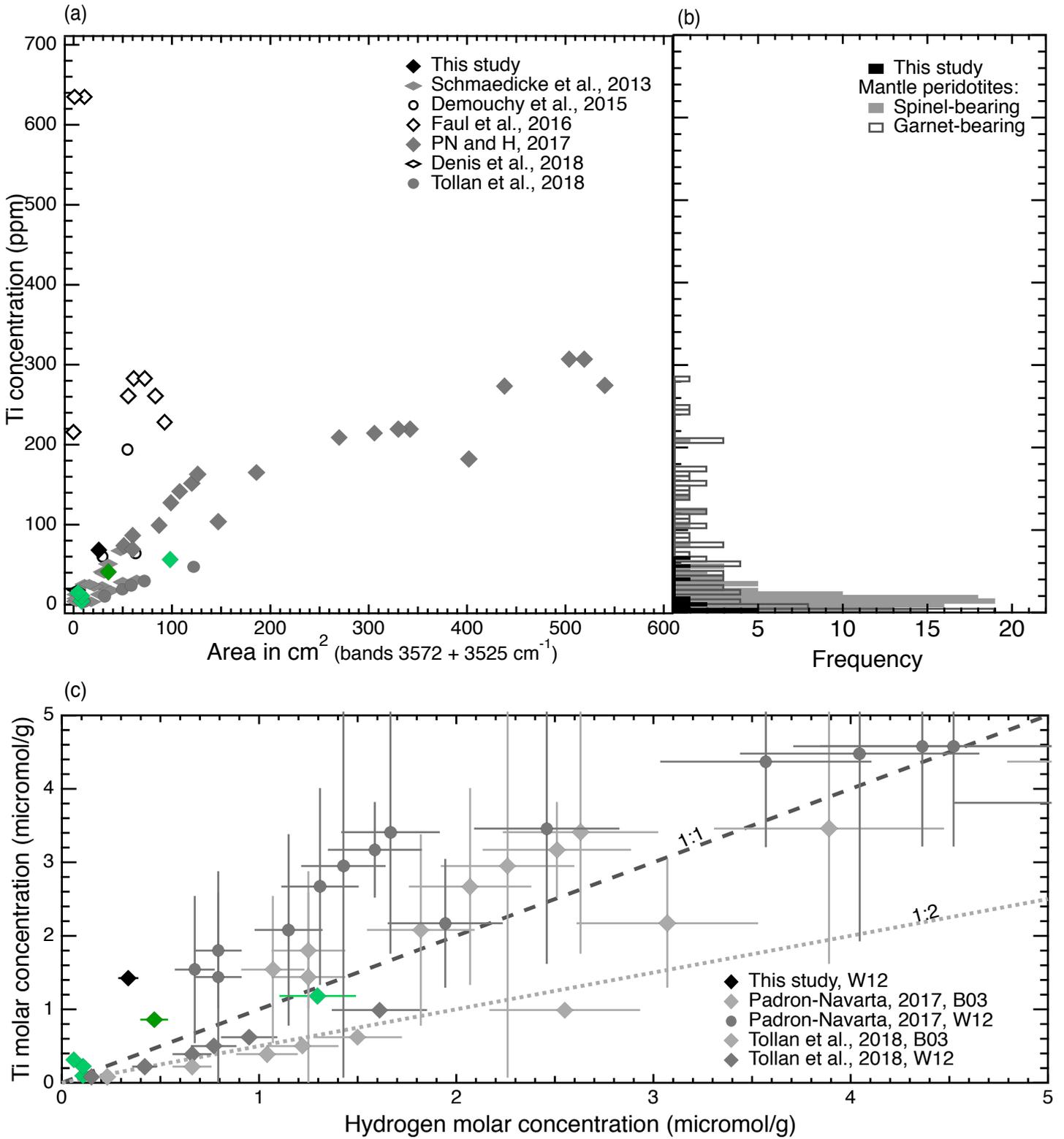




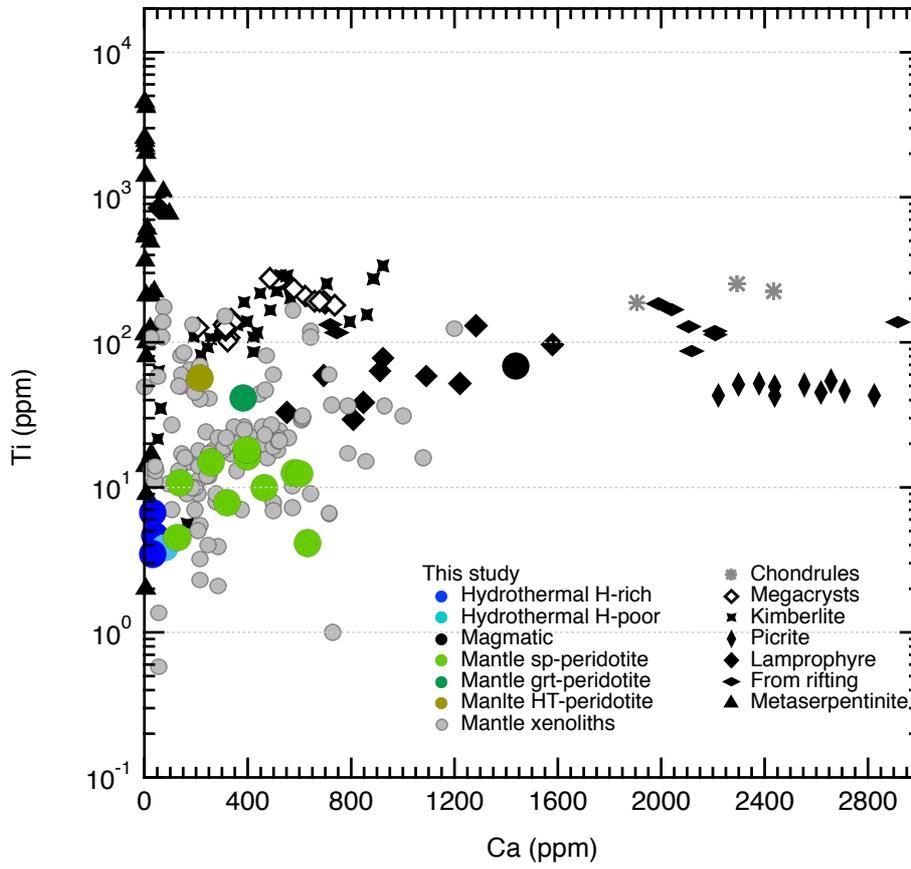
Demouchy and Alard, Fig. 8, Revised



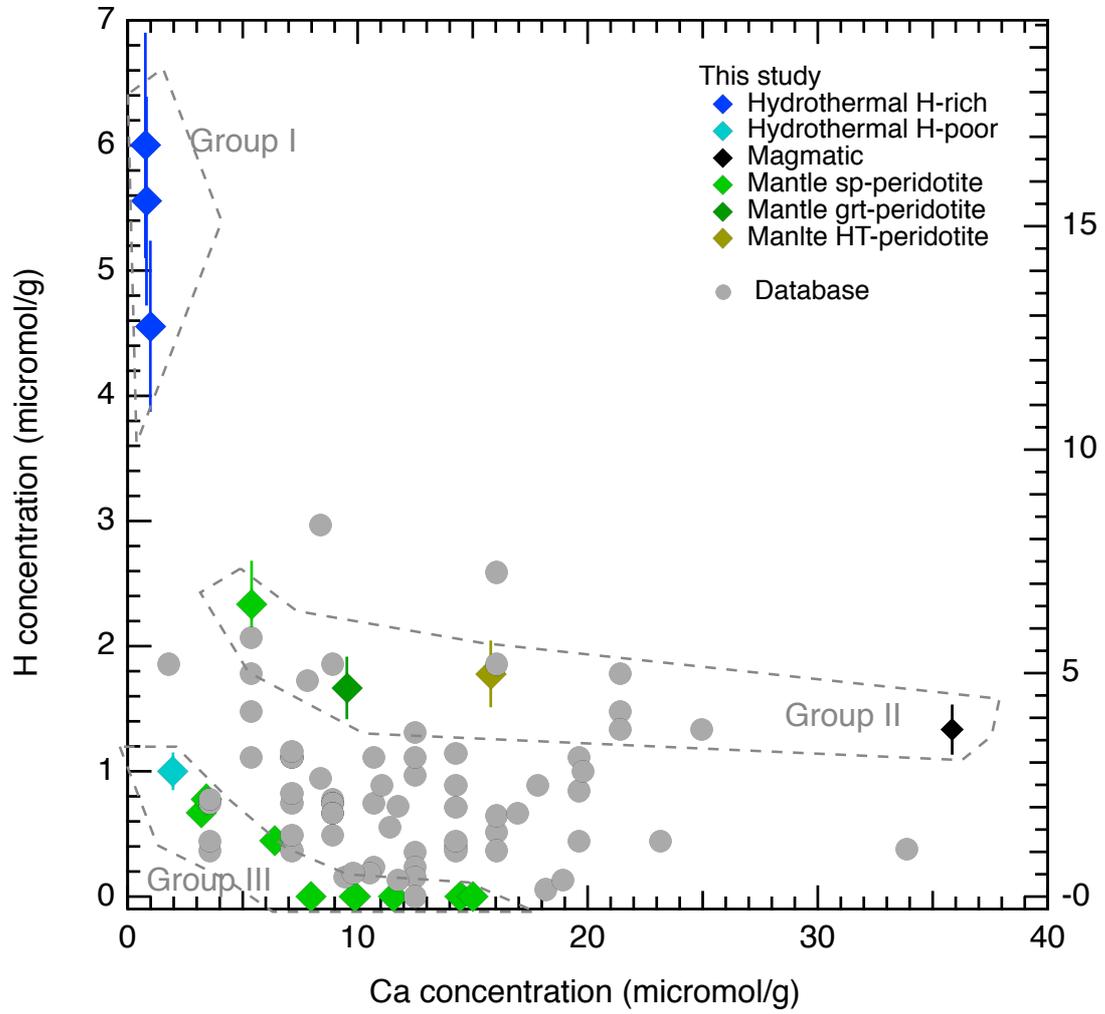




Demouchy and Alard, Fig. 11



Demouchy and Alard, Fig. 12, Revised



Demouchy and Alard, Fig. 13, Revised

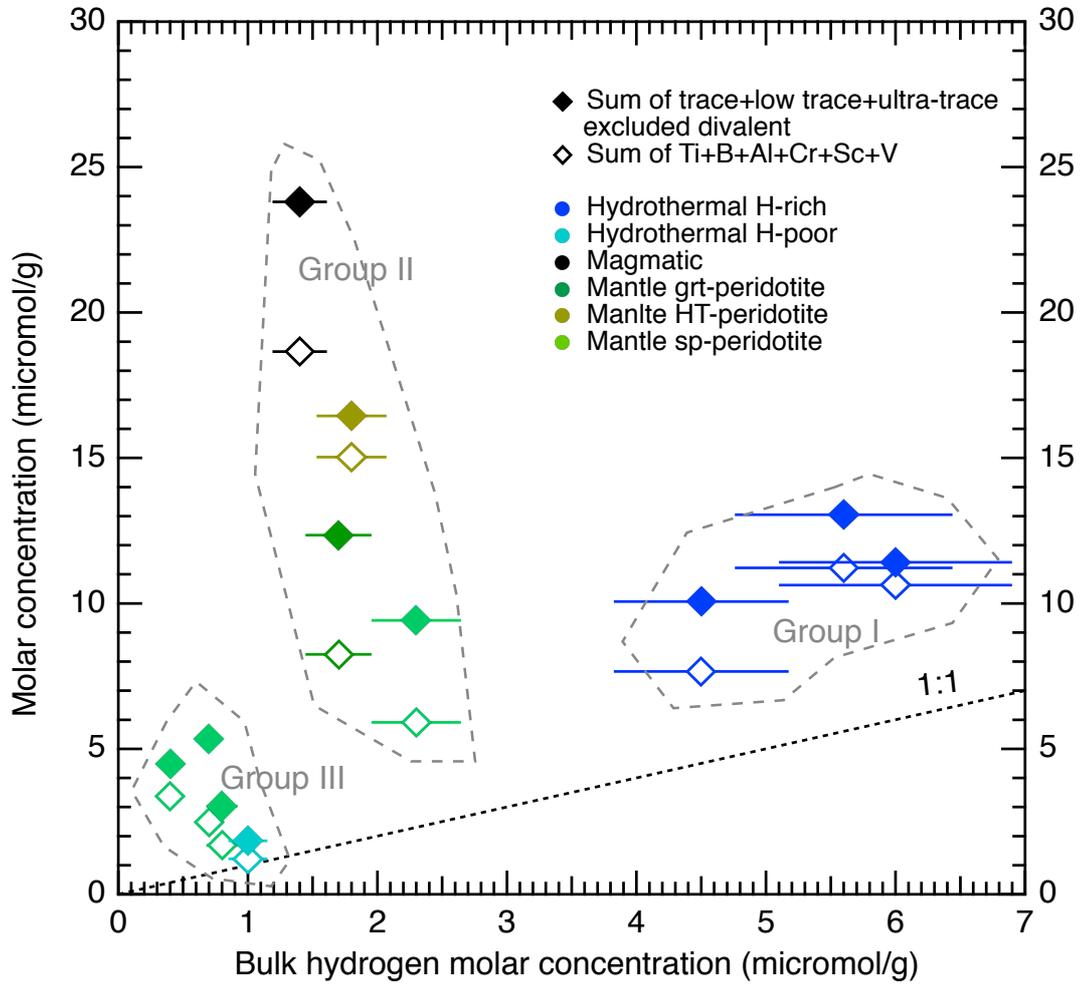


Table 1. Olivine prism sizes after sample preparation and OH band positions for each olivine specimen as identified by unpolarized FTIR.

		SAP	MYA	LR	OLM	NW1	NW2	SAS41	SAS20	SAS21	LAZ	PA3	DMP2	DMP4	HS1	PP	SC	SC2018			
Petrogenesis		Hydrothermal	Hydrothermal	Magmatic	Peridotite	Hydrothermal	Hydrothermal	HT Peridotite	Peridotite	Peridotite	Peridotite	Grt Peridotite	Peridotite	Peridotite	Peridotite	Peridotite	Peridotite	Peridotite	Peridotite		
Sample size		<i>Samples with detectable OH</i>											<i>No detectable OH</i>								
Length 1	(mm)	1.865	1.164	0.738	1.01	1.176	1.16	1.116	1.336	0.722	1.178	0.883	0.646	1.054	1.599	1.328	1.035	0.476			
Length 2	(mm)	3.154	1.565	1.17	1.411	1.482	1.485	1.794	1.485	0.803	1.731	0.98	1.126	1.91	1.627	1.398	1.825	2.457			
Length 3	(mm)	4.542	1.979	1.267	1.919	1.764	1.755	2.835	1.541	1.592	1.913	1.09	1.138	2.032	1.686	1.72	2.26	2.505			
Wavenumber ^{1,2}	(cm ⁻¹)																		Band assignment ³		
Range I	3698	x	o	o	o	x	x	o	o	o	o	o	o	o	o	o	o	o	o	Serpentine lamellae	
	3650	o	o	o	o	w	w	o	o	o	o	o	o	o	o	o	o	o	o	Serpentine lamellae	
	3598	x	x	o	o	x	x	o	x	o	3612	x	o	o	o	o	o	o	o	o	Ti vacancies
	3572	o	o	o	w	o	o	x	x	o	o	x	o	o	o	o	o	o	o	o	TiChu point defect
	3562	o	x	x	o	o	o	o	o	o	3568	o	o	o	o	o	o	o	o	o	Si vacancies ⁴
	3542	o	x	o	o	o	o	o	o	x	o	x	x	o	o	o	o	o	o	o	Si vacancies
Range II	3525	o	o	x	o	o	o	w	x	o	x	x	o	o	o	o	o	o	o	TiChu point defect	
	3485	x	3477	x	o	x	x	o	x	o	o	x	o	o	o	o	o	o	o	o	Si vacancies
	3402	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	TiChu lamellae
	3387	o	o	o	o	o	o	o	o	x	o	o	o	o	o	o	o	o	o	o	
	3355	o	o	x	x	o	o	w	x	x	x	x	o	o	o	o	o	o	o	o	Trivalent defects
	3327	o	o	x	x	o	o	w	x	x	x	x	o	o	o	o	o	o	o	o	Trivalent defects
3230	o	o	w	o	o	o	w	o	o	o	o	x	o	o	o	o	o	o	o	Mg vacancies	

¹ Wavenumber resolution ± 4 cm⁻¹.

² OH band presence is indicated as x = present, w = weak, or o = absent. When the expected band is offset but corresponds to the same defect, the wavenumber is indicated directly.

³ This compilation of OH band assignments in olivine is identical to Thoraval et al. (2019), and was previously established by Beran and Libowitzky (2006), Padrón-Navarta et al. (2014), and Jollands et al. (2015). Trivalent defect bands occur at 3353 cm⁻¹ for Fe³⁺, and 3358, 3328, and 3323 cm⁻¹ for Cr³⁺ (Jollands et al., 2016). 'TiChu point defect' indicates the Ti and H associated defect {Ti_{Mg}^{••}, (2H)_{Si}[']}_x, also called the titanium clinohumite-like point defect (Berry et al., 2005). TiChu lamellae = titanium clinohumite lamellae.

⁴ Overlapping with 3553 cm⁻¹ from TiChu point defects.

Table 2. Average major and minor element concentrations determined by semi-quantitative μ XRF for each olivine.

wt%	SAP	MYA	LR	OLM	NW1	NW2	SAS41	SAS20	SAS21	LAZ	PA3	DMP2	DMP4	HS1	PP	SC	SC2018	SCO-2 ($n=5$) ¹
SiO₂	40.47	41.40	37.90	41.13	41.30	41.29	40.22	40.51	40.52	40.31	40.09	40.03	40.10	40.04	39.96	39.90	40.02	40.62
TiO₂	-	-	0.01	-	-	-	-	0.01	-	-	0.01	-	-	-	0.00	-	-	0.00
Al₂O₃	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.00
Cr₂O₃	-	-	-	-	-	-	-	-	-	0.02	-	0.01	0.02	-	-	-	-	-
FeO	9.11	5.77	15.58	6.74	6.03	6.30	10.44	8.88	8.82	9.93	11.14	10.65	9.93	10.55	10.20	10.64	10.55	9.83
MnO	0.14	0.13	0.17	0.09	0.17	0.18	0.13	0.13	0.12	0.13	0.13	0.14	0.12	0.14	0.18	0.15	0.15	0.11
MgO	48.94	51.64	43.28	50.90	51.53	51.33	47.57	49.07	49.04	48.09	46.91	47.53	48.33	47.54	48.10	47.56	47.59	48.76
CaO	0.02	0.07	0.24	0.05	0.13	0.02	0.11	0.04	0.13	0.07	0.08	0.10	0.07	0.19	0.09	0.20	0.14	0.11
Na₂O	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NiO	0.36	0.42	0.38	0.42	0.23	0.24	0.43	0.43	0.45	0.43	0.47	0.42	0.41	0.43	0.38	0.43	0.44	0.43
Total	99.05	99.43	97.56	99.32	99.40	99.37	98.90	99.08	99.09	98.97	98.83	98.89	98.97	98.89	98.93	98.88	98.89	99.96*
O	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000
Si	1.000	1.003	0.979	1.002	1.002	1.003	1.001	1.000	1.000	1.000	1.002	0.998	0.996	0.998	0.995	0.996	0.998	0.998
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Al	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe	0.188	0.117	0.337	0.137	0.122	0.128	0.217	0.183	0.182	0.206	0.233	0.222	0.206	0.220	0.212	0.222	0.220	0.204
Mn	0.003	0.003	0.004	0.002	0.004	0.004	0.003	0.003	0.003	0.003	0.003	0.003	0.002	0.003	0.004	0.003	0.003	0.002
Mg	1.802	1.865	1.667	1.848	1.863	1.858	1.766	1.805	1.804	1.779	1.748	1.767	1.789	1.767	1.785	1.769	1.769	1.786
Ca	0.001	0.002	0.007	0.001	0.003	0.001	0.003	0.001	0.003	0.002	0.002	0.003	0.002	0.005	0.002	0.005	0.004	0.003
Na	0.000	0.000	0.019	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ni	0.007	0.008	0.008	0.008	0.004	0.005	0.009	0.008	0.009	0.009	0.009	0.009	0.008	0.009	0.008	0.009	0.009	0.009
Sum cations	3.000	2.997	3.021	2.998	2.998	2.997	2.999	3.000	3.000	2.999	2.998	3.002	3.004	3.002	3.005	3.004	3.002	3.002
Fo%²	90.54	94.11	83.20	93.09	93.84	93.56	89.04	90.78	90.83	89.62	88.25	88.83	89.67	88.93	89.37	88.85	88.94	89.75

¹ In-house Standard, San Carlos Olivine, Mcquarie University (see Table S1).² Fo% = 100 x Mg/(Fe+Mg).

* average of the 5 totals

Table 3. Hydrogen concentration in olivine specimens with detectable O-H only, and obtained by unpolarized ('unpo') and polarized ('po') FTIR using the frequency-dependent calibration of Paterson (1982; 'Pat') and the mineral-dependent calibration of Withers et al. (2012; 'W'). The average integrated absorbances normalized to sample thickness are compiled in Table S3, and integrations were performed in the 3650–3050 cm⁻¹ wavenumber range.

Sample #	[OH] unpo1Pat	[OH] po2Pat	[OH] po 3W	[OH] po triplet_1 4W	[OH] po triplet_2 5W
<i>Concentration in ppm H by weight (= molar concentration* in micro mole / g of olivine)</i>					
SAP	3.1	3.3	4.5	4.5	4.5
MYA	0.6	0.7	1.0	1.2	1.2
LR	0.6	0.7	1.4	1.5	1.3
OLM	0.3	0.3	0.7	0.9	0.6
NW1	3.2	4.3	6.0	5.5	6.4
NW2	3.6	4.0	5.6	5.5	5.6
SAS41	0.2	0.3	0.8	0.8	0.8
SAS20	1.4	1.3	2.3	2.5	2.5
SAS21	0.6	0.7	1.8	1.9	1.7
LAZ	0.1	0.3	0.4	0.5	0.4
PA3	0.8	1.0	1.7	1.7	1.7
<i>Concentration in ppm H₂O by weight</i>					
SAP	28	30	41	41	40
MYA	5	6	9	10	10
LR1	5	6	12	13	12
OLM	3	3	6	8	6
NW1	29	39	54	49	58
NW2	32	36	50	50	51
SAS41	2	3	7	7	7
SAS20	13	12	21	22	22
SAS21	5	6	16	17	15
LAZ	1	3	4	4	3
Pa3	7	9	15	15	15
<i>Concentration in H/10⁶ Si (= ppm H/Si)</i>					
SAP	456	489	663	667	659
MYA	80	96	137	168	168
LR1	84	101	210	224	198
OLM	48	48	98	125	92
NW1	466	627	860	793	927
NW2	515	579	804	796	813
SAS41	33	49	117	113	123
SAS20	212	195	343	364	366
SAS21	81	98	267	279	252
LAZ	16	49	64	72	56
Pa3	115	148	253	249	255

1: Calculated from the average of 3 perpendicular unpolarized spectra, and the application of the calibration of Paterson (1982).

2: Calculated from the average of all six polarized spectra, acquired from 3 faces perpendicular to each other, and then times by a factor 3, followed by the application of the Paterson's calibration (1982)

3: Calculated from the average of all six polarized spectra, acquired from 3 faces perpendicular to each other, and then times by a factor 3, followed by the application of the calibration of Withers et al., (2012)

4: Calculated from the summ of 3 polarized spectra perpendicular to each other (triplet 1) followed by the application of the calibration of Withers et al., (2012)

5: Calculated from the summ of 3 polarized spectra perpendicular to each other (triplet 2) followed by the application of the calibration of Withers et al., (2012)

* Since the molar weight of hydrogen equals 1, this is also giving the molar weight

Table 4. Minor, trace, and ultra-trace element concentrations (ppm) measured by LA-ICP-MS analyses of the olivine specimens (*n* is the number of the measurements and $\pm 1SD$ the standard deviation; typical detection limits for each element are given in Table S2).

<i>ppm</i>	SAP	<i>n</i> = 5	MYA	<i>n</i> = 5	LR	<i>n</i> = 5	OLM	<i>n</i> = 5	NW1	<i>n</i> = 5	NW2	<i>n</i> = 5	SAS41	<i>n</i> = 5	SAS20	<i>n</i> = 5	SAS21	<i>n</i> = 5
	<i>Avg</i>	$\pm 1SD$																
Li	12.61	1.06	0.71	0.06	1.89	0.05	1.32	0.11	1.73	0.39	9.02	0.45	1.61	0.05	2.32	0.08	1.34	0.04
Be	0.0067	0.0069	0.0015	0.0007	BDL	BDL	0.0037	0.0000	0.0030	-	BDL	BDL	BDL	BDL	BDL	BDL	0.0018	0.0002
B	61.26	6.64	2.96	0.18	1.29	0.06	1.31	0.07	101.38	3.95	109.45	7.89	1.22	0.04	1.44	0.09	1.24	0.03
Na	0.30	0.22	3.55	0.48	58.19	0.99	51.79	4.56	0.16	0.11	0.08	0.04	11.61	0.12	51.91	0.67	17.68	0.37
Al	0.92	0.33	13.00	0.61	224.90	8.70	8.24	0.34	0.66	0.03	0.66	0.03	21.00	0.34	52.22	0.71	155.92	4.85
P	17.09	1.20	10.72	1.04	71.52	1.26	12.22	0.98	15.92	0.87	16.00	2.08	18.29	0.48	27.62	1.41	13.65	0.60
Ca	40	3	79	7	1437	61	128	15	31	2	33	2	137	10	216	6	633	37
Sc	6.38	0.60	2.39	0.01	2.58	0.05	1.96	0.03	8.71	0.93	6.00	0.99	1.94	0.02	2.20	0.02	2.34	0.03
Ti	4.63	0.23	3.83	0.11	68.21	1.37	4.48	0.29	6.66	0.29	3.46	0.29	10.80	0.29	56.60	0.29	4.14	0.29
V	0.81	0.08	0.55	0.02	6.86	0.10	0.92	0.06	0.14	0.01	0.15	0.04	1.33	0.03	2.79	0.05	6.16	0.10
Cr	74.0	12.6	11.3	0.3	440.8	6.4	94.8	14.4	26.0	1.2	30.7	8.6	21.3	0.3	127.8	1.1	456.1	6.0
Mn	1119	16	937	16	1390	20	706	2	1375	22	1377	50	1084	16	979	8	997	8
Co	139.6	1.9	138.4	3.2	170.6	3.0	124.7	1.0	157.3	2.0	159.1	2.4	146.8	1.2	139.9	2.5	144.4	2.4
Ni	2676	16	3228	76	2742	52	3078	26	1697	30	1699	37	3091	12	3133	26	3229	40
Cu	0.13	0.07	0.54	0.01	4.24	0.11	0.39	0.02	0.011	0.007	0.005	0.002	0.47	0.01	0.46	0.05	2.13	0.02
Zn	21.00	0.54	38.88	0.96	91.51	2.19	34.68	0.40	15.52	0.35	16.08	0.26	38.86	0.44	50.80	0.63	48.73	0.66
Ga	0.0102	0.0031	0.0075	0.0012	0.1708	0.0131	0.0117	0.0019	0.0095	0.0019	0.0096	0.0021	0.0146	0.0028	0.0343	0.0066	0.0446	0.0046
Ge	1.38	0.05	0.96	0.07	1.75	0.06	0.91	0.03	0.98	0.06	1.04	0.05	1.35	0.05	1.13	0.03	1.17	0.05
Rb	0.0133	0.0080	0.0020	0.0004	BDL	BDL	0.0024	0.0004	0.0034	BDL	BDL	BDL	BDL	BDL	0.0024	0.0006	0.0032	0.0011
Sr	0.0019	0.0016	0.0006	0.0003	0.0046	0.0015	0.0100	0.0072	0.0010	0.0013	0.0005	BDL	0.0013	0.0009	0.0006	0.0004	0.0474	0.0011
Y	0.0424	0.0050	0.0012	0.0004	0.1055	0.0056	0.0353	0.0043	0.0484	0.0019	0.0472	0.0180	0.0080	0.0011	0.0093	0.0014	0.0014	0.0003
Zr	0.0073	0.0025	0.0053	0.0023	0.0562	0.0036	0.0191	0.0049	0.0028	0.0010	0.0006	0.0003	0.0007	0.0004	0.3390	0.0210	0.0070	0.0009
Nb	0.0017	0.0010	0.0010	0.0007	0.0003	0.0002	0.0286	0.0156	0.0004	0.0002	BDL	BDL	0.0002	-	0.0235	0.0032	0.0086	0.0022
Mo	0.0216	0.0079	0.0107	0.0021	0.0156	0.0031	0.0065	0.0034	0.0158	0.0035	0.0158	0.0049	0.0156	0.0074	0.0149	0.0043	0.0126	0.0024
Cs	0.0056	0.0042	BDL	BDL	BDL	BDL	0.0007	0.0001	BDL	BDL								
Ba	0.0156	0.0099	0.0023	0.0013	0.0004	0.0001	0.0039	0.0035	0.0019	0.0015	0.0015	0.0006	0.0035	0.0034	0.0017	0.0013	0.0028	0.0014
La	0.00125	0.00095	0.00019	0.00017	0.00019	0.00009	0.00119	0.00120	0.00057	0.00060	BDL	BDL	0.00013	0.00008	0.00011	0.00004	0.00013	0.00012
Ce	0.0034	0.0010	0.0004	0.0003	0.0003	0.0002	0.0020	0.0021	0.0001	0.0000	0.0001	0.0000	0.0001	0.0001	0.0003	0.0001	0.0003	0.0001
Pr	0.00943	0.00912	BDL	BDL	0.00008	0.00002	0.00028	0.00025	0.00010	0.00009	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Nd	0.00560	0.00315	BDL	BDL	0.00061	0.00023	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.00034	0.00014	0.00053	0.00039
Sm	0.00133	0.00064	BDL	BDL	0.00065	0.00022	0.00039	0.00026	BDL	BDL								
Eu	0.00169	0.00184	BDL	BDL	0.00055	0.00021	0.00023	0.00015	BDL	BDL	BDL	BDL	BDL	BDL	0.00010	0.00003	0.00008	0.00003
Gd	0.00397	0.00263	0.00029	0.00011	0.00316	0.00030	0.00093	0.00042	BDL	BDL	0.00025	0.00008	BDL	BDL	0.00048	0.00029	0.00033	0.00017
Tb	0.00040	0.00009	0.00005	0.00003	0.00104	0.00028	0.00035	0.00016	0.00010	0.00007	0.00006	0.00003	BDL	BDL	0.00012	0.00004	0.00005	0.00003
Dy	0.00428	0.00117	0.00024	0.00008	0.01210	0.00202	0.00443	0.00069	0.00172	0.00073	0.00046	0.00016	0.00036	0.00022	0.00105	0.00055	0.00044	0.00040
Ho	0.00251	0.00066	0.00013	0.00010	0.00358	0.00042	0.00119	0.00050	0.00132	0.00028	0.00117	0.00023	0.00021	0.00014	0.00026	0.00008	0.00017	0.00011
Er	0.0153	0.0023	0.0006	0.0006	0.0138	0.0020	0.0055	0.0009	0.0135	0.0030	0.0145	0.0046	0.0012	0.0003	0.0013	0.0003	0.0005	0.0004
Tm	0.00620	0.00085	0.00007	0.00002	0.00260	0.00049	0.00124	0.00013	0.00515	0.00068	0.00532	0.00117	0.00041	0.00005	0.00031	0.00016	0.00010	0.00005
Yb	0.0710	0.0130	0.0014	0.0010	0.0277	0.0039	0.0114	0.0019	0.0583	0.0076	0.0576	0.0057	0.0054	0.0015	0.0030	0.0004	0.0011	0.0003
Lu	0.01333	0.00356	0.00044	0.00014	0.00540	0.00111	0.00222	0.00024	0.01473	0.00362	0.01288	0.00149	0.00223	0.00050	0.00045	0.00012	0.00025	0.00009
Hf	0.00222	0.00214	0.00048	0.00026	0.00145	0.00089	0.00029	0.00016	0.00037	0.00027	BDL	BDL	0.00027	0.00015	0.00553	0.00159	0.00045	0.00043
Ta	0.00280	0.00180	0.00008	0.00008	0.00146	0.00049	0.00252	0.00219	0.00128	0.00104	0.00037	0.00025	0.00835	0.00766	0.00162	0.00064	0.00727	0.00658
Pb	0.0313	0.0395	0.0130	0.0137	0.0039	0.0017	0.0032	0.0014	0.0041	0.0018	0.0087	0.0071	0.0061	0.0033	0.0043	0.0019	0.0044	0.0031
Bi	0.01501	0.00789	0.00067	0.00031	0.00060	0.00024	0.00199	0.00154	0.00180	0.00104	0.00140	0.00052	0.00127	0.00117	0.00157	0.00137	0.00042	0.00041
Th	0.00162	0.00129	0.00030	0.00010	BDL	BDL	0.00085	0.00105	0.00018	0.00018	0.00021	0.00023	0.00013	0.00007	0.00029	0.00029	0.00025	0.00018
U	0.00526	0.00408	0.00028	0.00023	0.00013	0.00006	0.00060	0.00077	0.00028	0.00043	0.00013	0.00009	0.00009	0.00002	0.00014	0.00008	0.00016	0.00011

Table 4 (continued)

	LAZ	<i>n</i> = 5	Pa3	<i>n</i> = 5	DMP2	<i>n</i> = 5	DMP4	<i>n</i> = 5	HS1	<i>n</i> = 5	PP	<i>n</i> = 5	SC	<i>n</i> = 5	SC2018	<i>n</i> = 5	SCO-1	<i>n</i> = 6
<i>ppm</i>	Avg	\pm ISD																
Li	1.37	0.05	2.00	0.11	1.57	0.10	1.77	0.05	3.72	0.10	1.78	0.04	1.59	0.05	1.62	0.06	1.77	0.10
Be	BDL	BDL	0.0027	0.0019	BDL	BDL	BDL	BDL	0.0036	0.0021	0.0021	0.0010	0.0022	0.0019	BDL	BDL	BDL	BDL
B	2.18	0.19	1.30	0.10	1.89	0.16	1.38	0.10	1.84	0.11	1.56	0.13	1.16	0.11	1.34	0.06	1.36	0.11
Na	10.09	0.34	63.74	1.79	28.51	0.71	30.41	0.90	74.61	1.92	55.77	1.13	19.41	0.63	19.36	0.32	41.58	3.13
Al	43.15	1.31	120.39	4.78	96.46	7.30	59.13	1.26	84.88	4.28	96.94	2.90	93.09	1.35	94.69	1.99	72.95	1.26
P	13.68	1.28	31.56	3.32	19.03	1.08	11.41	0.60	12.81	0.32	37.01	1.41	21.67	0.69	22.23	0.70	11.14	0.87
Ca	257	14	382	7	397	22	319	14	464	23	396	28	580	26	601	31	436	31
Sc	3.17	0.10	2.10	0.03	3.03	0.04	3.09	0.07	3.00	0.07	2.62	0.04	2.40	0.03	2.42	0.02	2.53	0.16
Ti	14.92	0.44	41.16	1.04	16.39	0.65	7.79	0.25	9.97	0.25	18.20	0.25	12.51	0.25	12.39	0.25	9.30	0.46
V	1.91	0.06	4.95	0.05	3.42	0.10	3.27	0.05	4.07	0.04	3.42	0.05	3.00	0.06	2.93	0.06	3.07	0.04
Cr	52.6	0.9	133.4	0.8	80.4	2.5	132.3	3.7	223.3	5.9	132.6	1.0	163.4	2.6	160.8	1.7	136.7	1.6
Mn	1027	6	985	12	1065	28	1071	26	1070	31	1068	14	1145	12	1133	7	1017	17
Co	149.2	1.1	150.0	2.9	144.2	3.2	149.2	4.9	143.2	3.3	142.1	2.1	151.6	1.3	150.7	2.4	145.6	1.6
Ni	3306	9	3169	55	3049	60	3093	84	3070	98	2960	33	2949	36	2924	28	3112	42
Cu	1.05	0.01	3.03	0.09	1.35	0.09	1.39	0.05	0.33	0.01	2.11	0.05	1.50	0.03	1.49	0.02	0.85	0.02
Zn	1.05	0.01	67.50	1.66	1.35	0.09	1.39	0.05	0.33	0.01	48.70	1.13	50.61	1.31	50.42	0.68	50.38	0.47
Ga	0.0270	0.0042	0.1193	0.0080	0.0398	0.0025	0.0301	0.0026	0.0472	0.0068	0.0466	0.0039	0.0402	0.0052	0.0430	0.0043	0.0338	0.0030
Ge	1.38	0.03	1.25	0.03	1.27	0.05	1.44	0.07	1.60	0.04	1.38	0.05	1.61	0.08	1.59	0.04	1.34	0.04
Rb	0.0031	0.0024	BDL	BDL	BDL	BDL	BDL	BDL	0.0031	0.0022	0.0025	0.0013	0.0016	0.0004	0.0021	0.0006	0.0019	0.0003
Sr	0.0014	0.0006	0.0013	0.0012	0.0004	0.0003	0.0007	0.0004	0.0058	0.0005	0.0036	0.0015	0.0011	0.0005	0.0021	0.0012	0.0007	0.0003
Y	0.0032	0.0013	0.0066	0.0012	0.0226	0.0019	0.0068	0.0010	0.0149	0.0026	0.0276	0.0027	0.0091	0.0017	0.0084	0.0024	0.0315	0.0016
Zr	0.1415	0.0746	0.0156	0.0020	0.0041	0.0006	0.0091	0.0009	0.0480	0.0117	0.0953	0.0876	0.0151	0.0042	0.0158	0.0045	0.0638	0.0039
Nb	0.0058	0.0019	0.0061	0.0011	0.0010	0.0004	0.0012	0.0002	0.0055	0.0016	0.0076	0.0010	0.0013	0.0003	0.0012	0.0003	0.0021	0.0010
Mo	0.0212	0.0126	0.0118	0.0035	0.0113	0.0028	0.0134	0.0016	0.0158	0.0033	0.0137	0.0028	0.0129	0.0063	0.0136	0.0015	0.0094	0.0020
Cs	0.0010	0.0006	BDL	BDL	BDL	BDL	BDL	BDL	0.0012	0.0007	0.0013	0.0001	0.0010	BDL	BDL	BDL	BDL	BDL
Ba	0.0044	0.0022	0.0017	0.0010	0.0020	0.0020	0.0081	0.0082	0.0023	0.0017	0.0018	0.0010	0.0023	0.0015	0.0012	0.0005	0.0032	0.0012
La	0.00115	0.00181	0.00030	0.00018	0.00025	0.00015	0.00009	0.00004	0.00103	0.00149	0.00049	0.00033	0.00037	0.00037	0.00021	0.00018	0.00031	0.00041
Ce	0.0023	0.0021	0.0002	0.0001	0.0001	0.0000	0.0001	0.0000	0.0004	0.0003	0.0005	0.0003	0.0002	0.0001	0.0002	0.0001	0.0006	0.0007
Pr	0.00021	0.00017	0.00006	0.00002	0.00008	0.00004	BDL	BDL	0.00016	0.00013	0.00008	0.00002	BDL	BDL	0.00005	0.00002	0.00006	0.00003
Nd	0.0010	0.0006	0.00083	0.00105	0.0008	0.0001	0.0003	0.0001	0.00074	0.00064	0.00059	0.00044	0.00025	0.00011	0.00039	0.00012	0.0003	0.0001
Sm	0.00038	0.00026	BDL	BDL	BDL	BDL	BDL	BDL	0.00046	0.00027	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Eu	0.00014	0.00006	BDL	BDL	BDL	BDL	BDL	BDL	0.00018	0.00010	0.00023	0.00015	BDL	BDL	BDL	BDL	0.00010	0.00004
Gd	0.00075	0.00069	BDL	BDL	BDL	BDL	BDL	BDL	0.00074	0.00019	0.00077	0.00068	0.00029	0.00014	0.00024	0.00015	0.00046	0.00040
Tb	0.00013	0.00007	BDL	BDL	0.00010	0.00005	0.00012	0.00010	0.00023	0.00006	0.00020	0.00020	BDL	BDL	BDL	BDL	0.00019	0.00015
Dy	0.00115	0.00082	0.00042	0.00023	0.00116	0.00029	0.00046	0.00019	0.00278	0.00189	0.00252	0.00112	0.00070	0.00054	0.00029	0.00021	0.00217	0.00096
Ho	0.00026	0.00011	0.00011	0.00005	0.00081	0.00026	0.00016	0.00010	0.00059	0.00010	0.00075	0.00021	0.00017	0.00009	0.00017	0.00008	0.00085	0.00033
Er	0.0011	0.0007	0.0005	0.0002	0.0038	0.0008	0.0009	0.0002	0.0030	0.0008	0.0053	0.0014	0.0011	0.0002	0.0012	0.0006	0.0049	0.0014
Tm	0.00027	0.00022	0.00010	0.00004	0.00077	0.00021	0.00050	0.00014	0.00070	0.00037	0.00090	0.00018	0.00047	0.00010	0.00026	0.00016	0.00109	0.00018
Yb	0.0030	0.0010	0.0014	0.0011	0.0143	0.0025	0.0046	0.0013	0.0058	0.0017	0.0105	0.0029	0.0069	0.0007	0.0048	0.0019	0.0092	0.0020
Lu	0.00105	0.00035	0.00042	0.00033	0.00335	0.00059	0.00138	0.00024	0.00209	0.00051	0.00382	0.00090	0.00144	0.00012	0.00135	0.00027	0.00291	0.00097
Hf	0.00553	0.00441	0.00094	0.00126	BDL	BDL	BDL	BDL	0.00082	0.00026	0.00264	0.00291	0.00032	0.00013	0.00049	0.00035	0.00144	0.00095
Ta	0.00239	0.00138	0.00053	0.00022	0.00101	0.00080	0.00651	0.00409	0.00280	0.00184	0.00180	0.00090	0.00062	0.00057	0.00057	0.00050	0.00029	0.00022
Pb	0.0047	0.0017	0.0064	0.0029	0.0042	0.0021	0.0031	0.0016	0.0059	0.0044	0.0032	0.0012	0.0052	0.0049	0.0029	0.0004	0.0251	0.0095
Bi	0.00146	0.00106	0.00182	0.00135	0.00090	0.00042	0.00035	0.00021	0.00389	0.00258	0.00134	0.00056	0.00145	0.00125	0.00074	0.00046	0.00057	0.00039
Th	0.00107	0.00103	0.00024	0.00023	0.00006	0.00005	0.00004	0.00004	0.00034	0.00022	0.00026	0.00032	0.00033	0.00031	BDL	BDL	0.00022	0.00021
U	0.00236	0.00261	0.00079	0.00050	0.00024	0.00021	BDL	BDL	0.00043	0.00038	0.00032	0.00030	BDL	BDL	BDL	BDL	BDL	BDL

Hydrogen, trace and ultra-trace elements distribution in natural olivines

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Supplementary materials

Fig. 1S. (a) Photography of olivine specimens during cutting and polishing preparations step, from left to right, Norway, Sapat, San Carlos#1, #2, #3, La Réunion ; (b) Olivine specimens glue on glass section prior to X-ray fluorescence mapping and Laser ablation inductively coupled plasma mass spectrometry. One square is 5 mm.

(a)



(b)

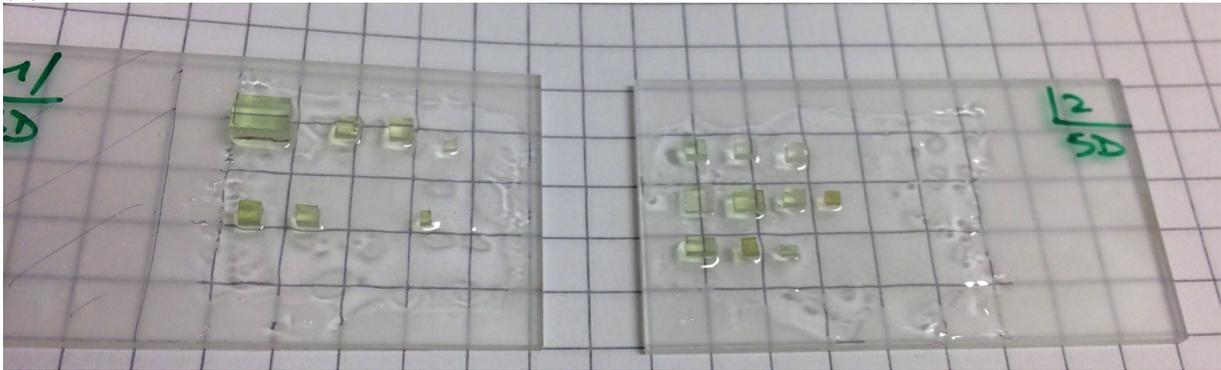
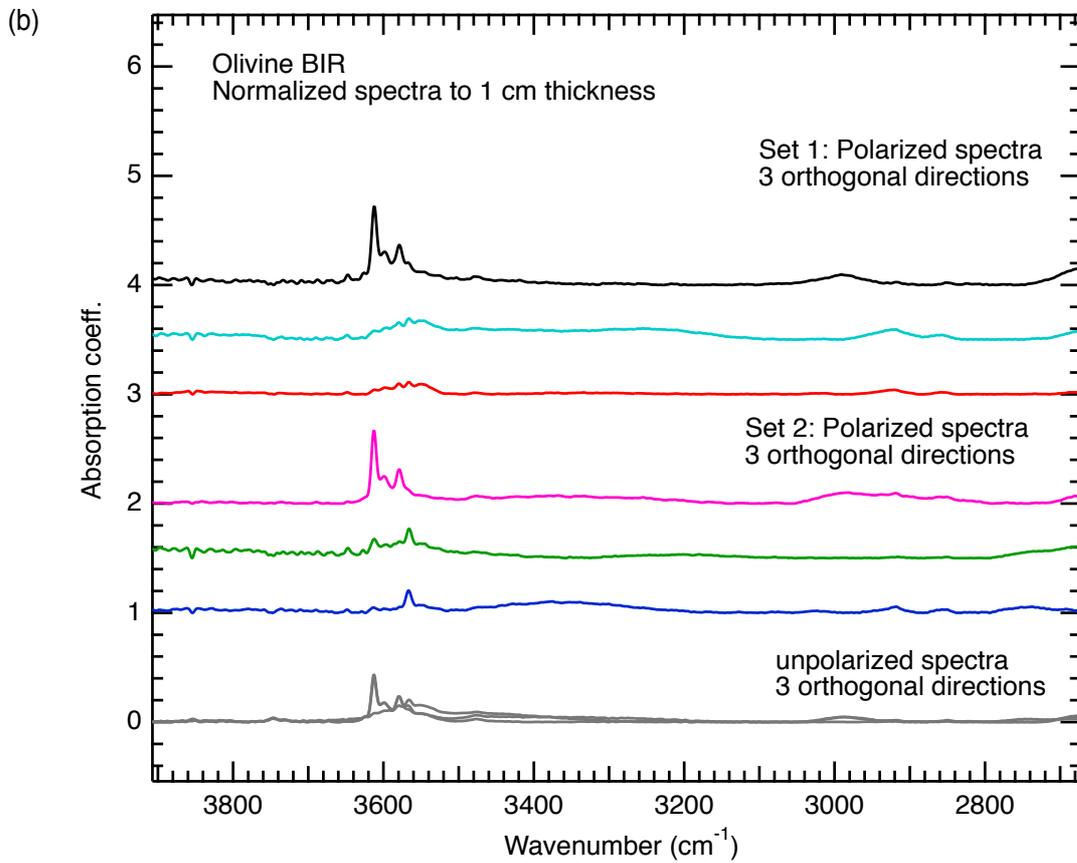
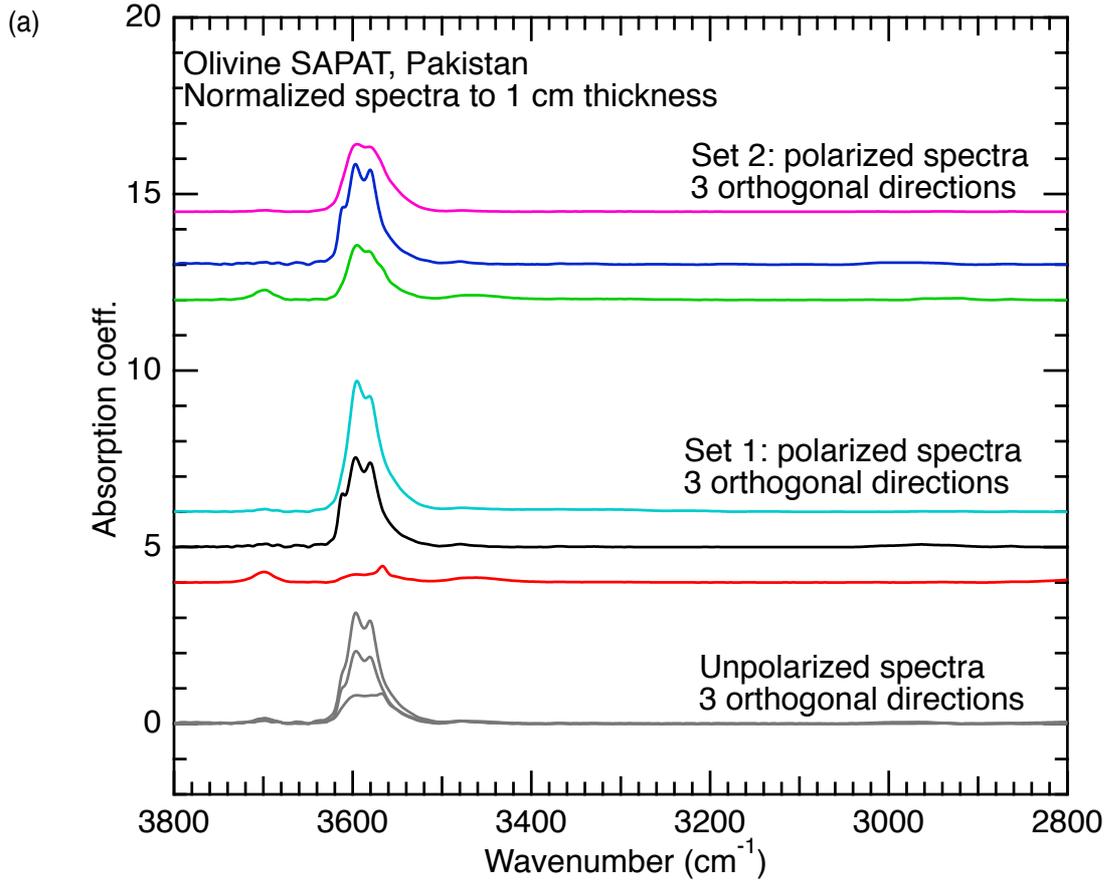
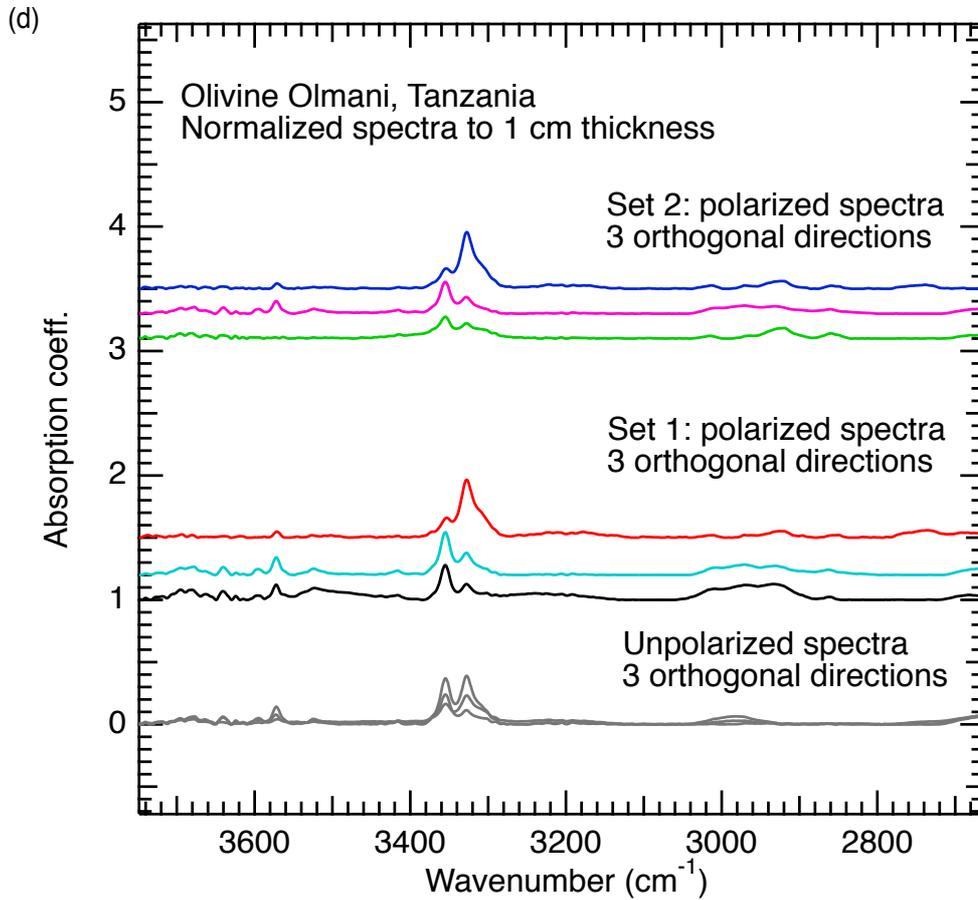
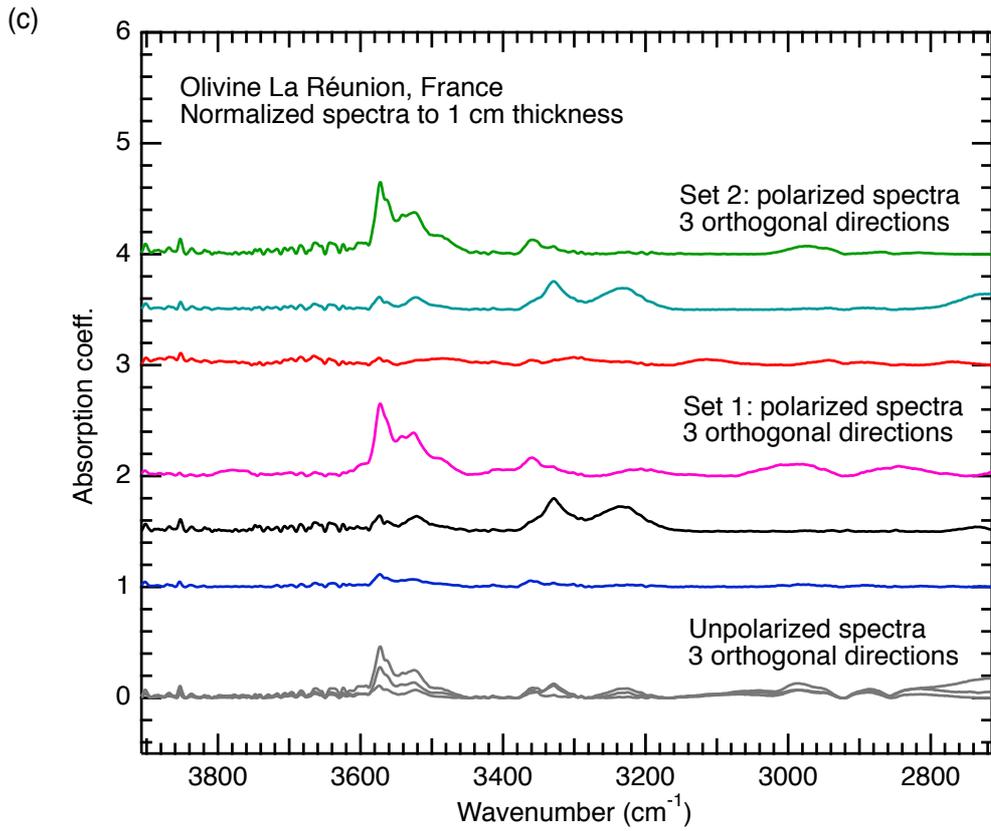
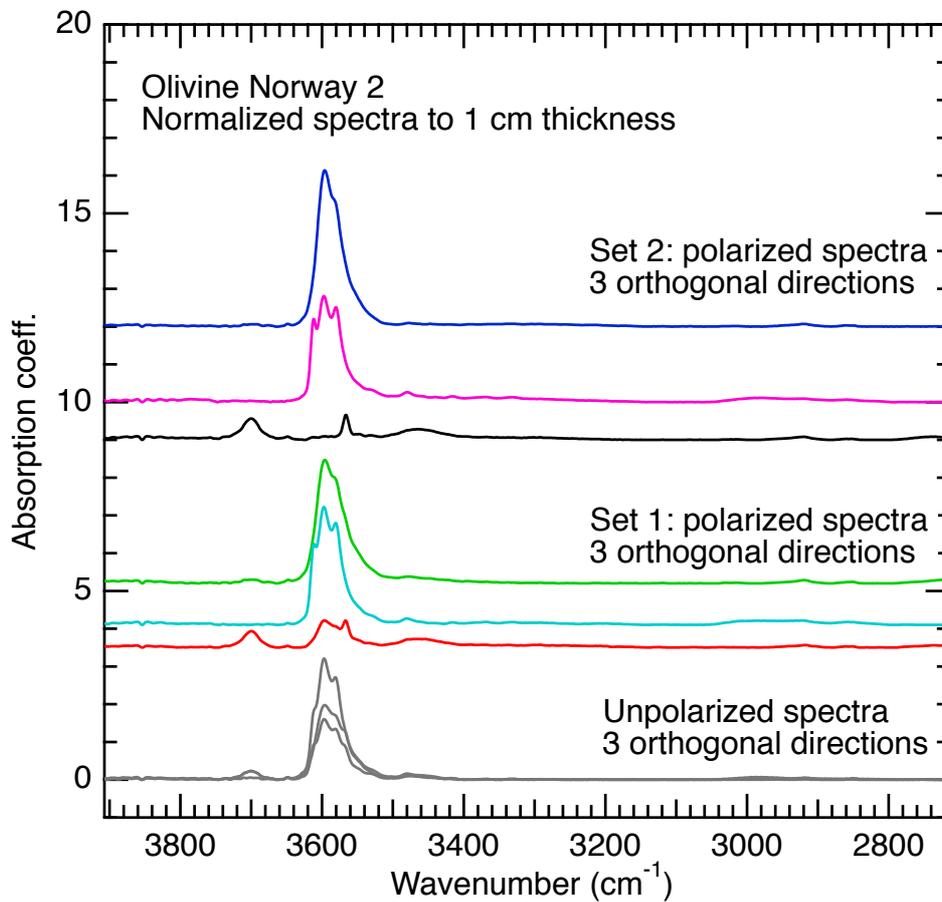
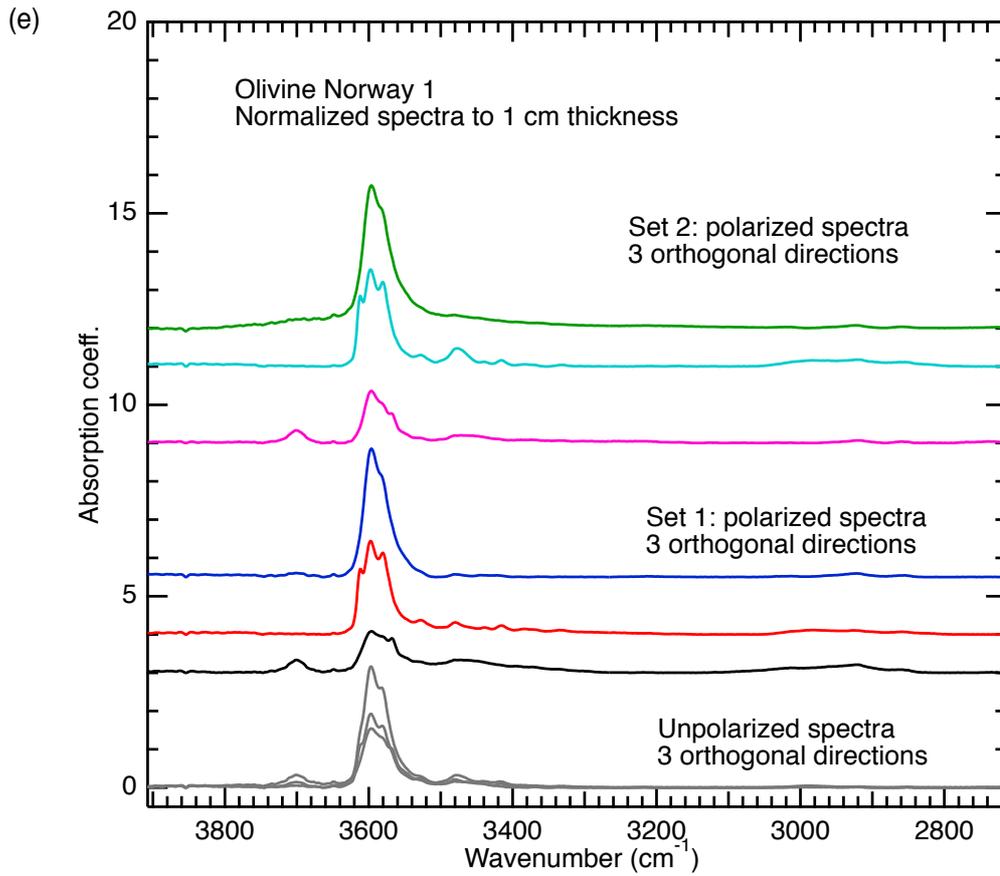
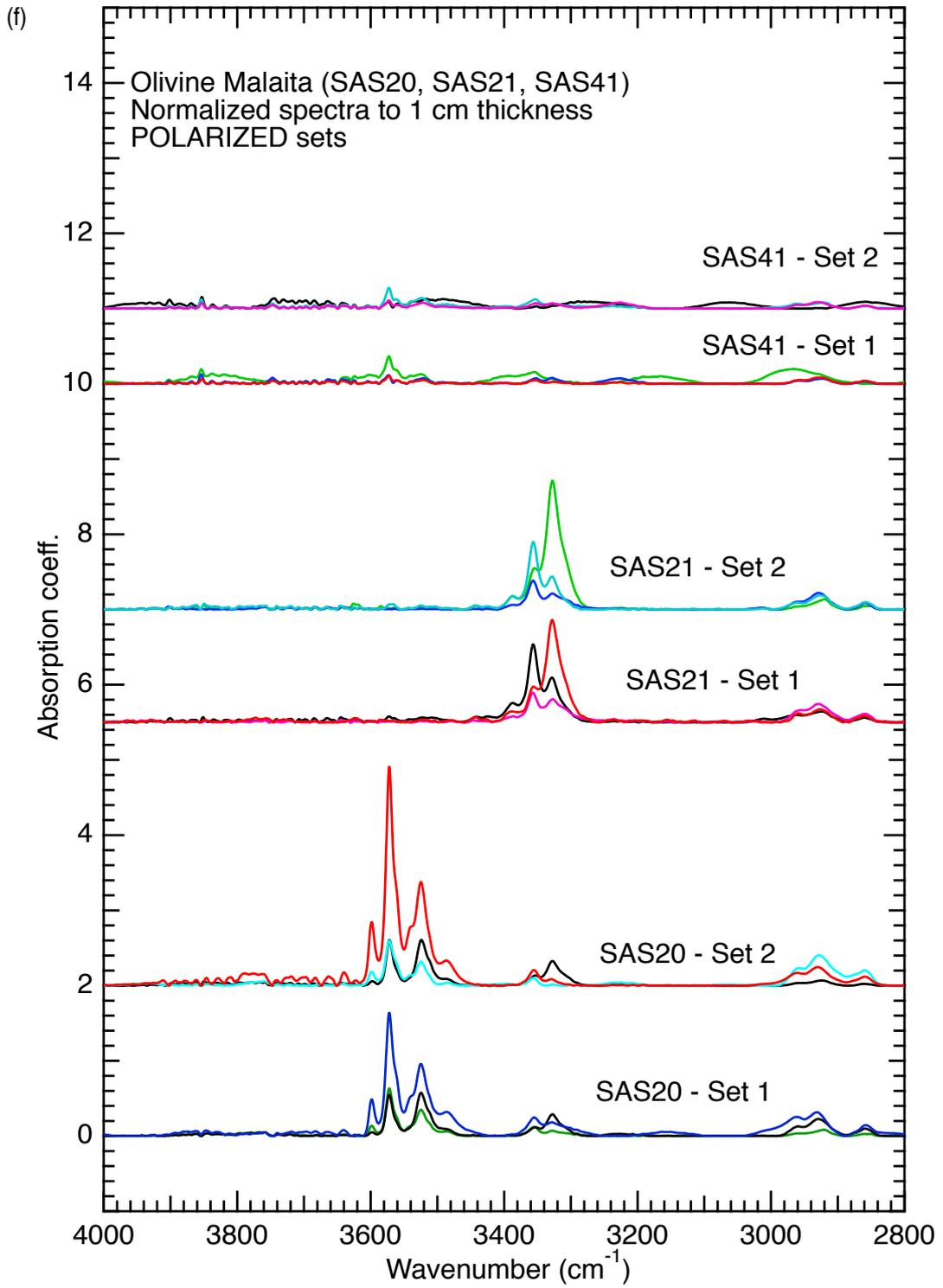


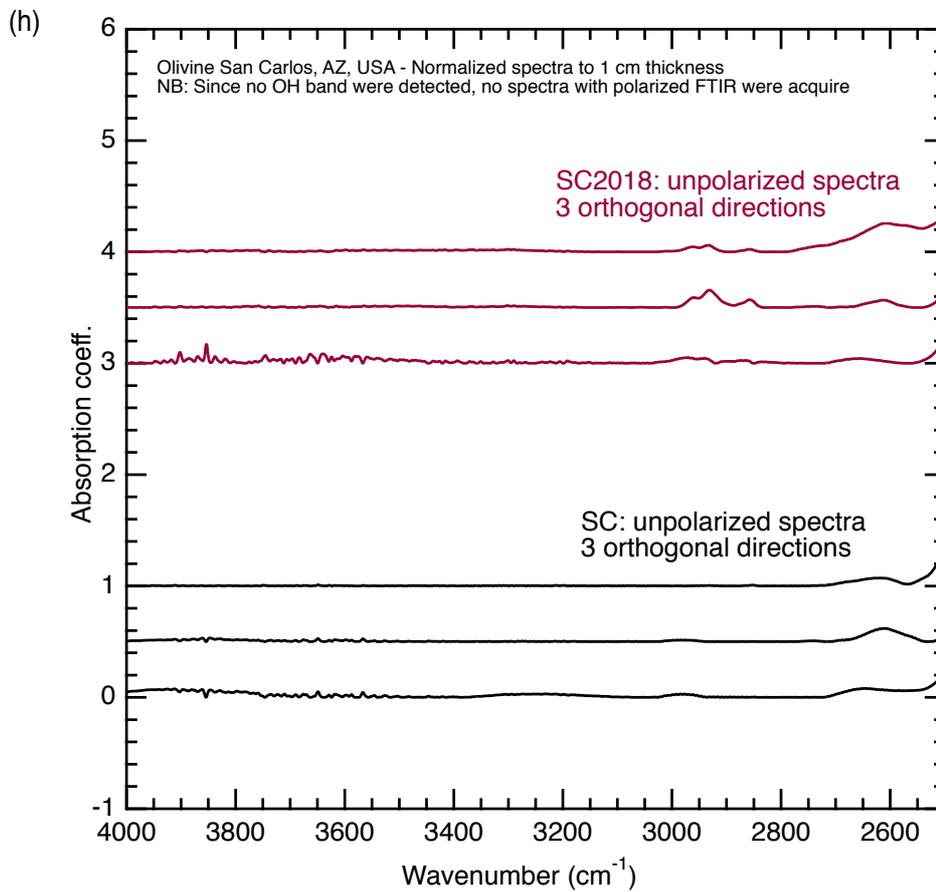
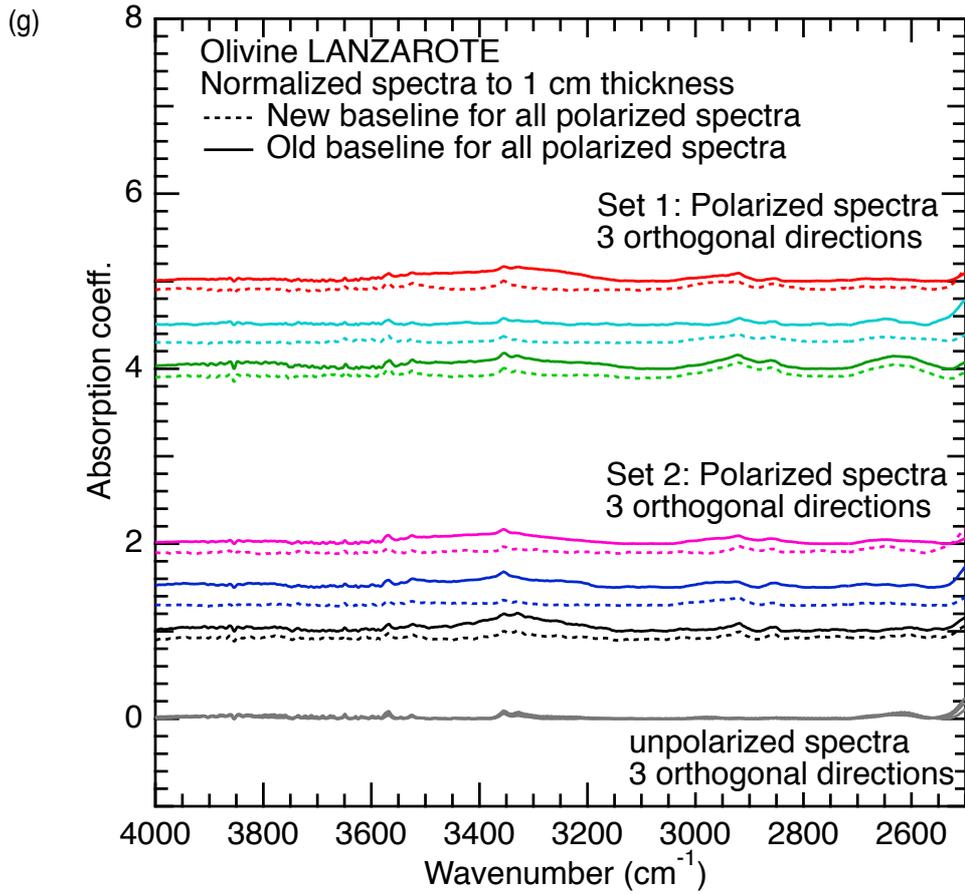
Fig. S2. Sets of FTIR spectra of olivines not presented in the main text: (a) SAP, (b) MYA, (c) LR, (d) OLM, (e) NW1 and NW2, (f) SAS41, SAS20, and SAS21, (g) LAZ, (h) SC2018 and SC, and (i) HS1, PP, and DMP. All spectra are normalized to 1 cm thickness.











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Fig S1. (continued)

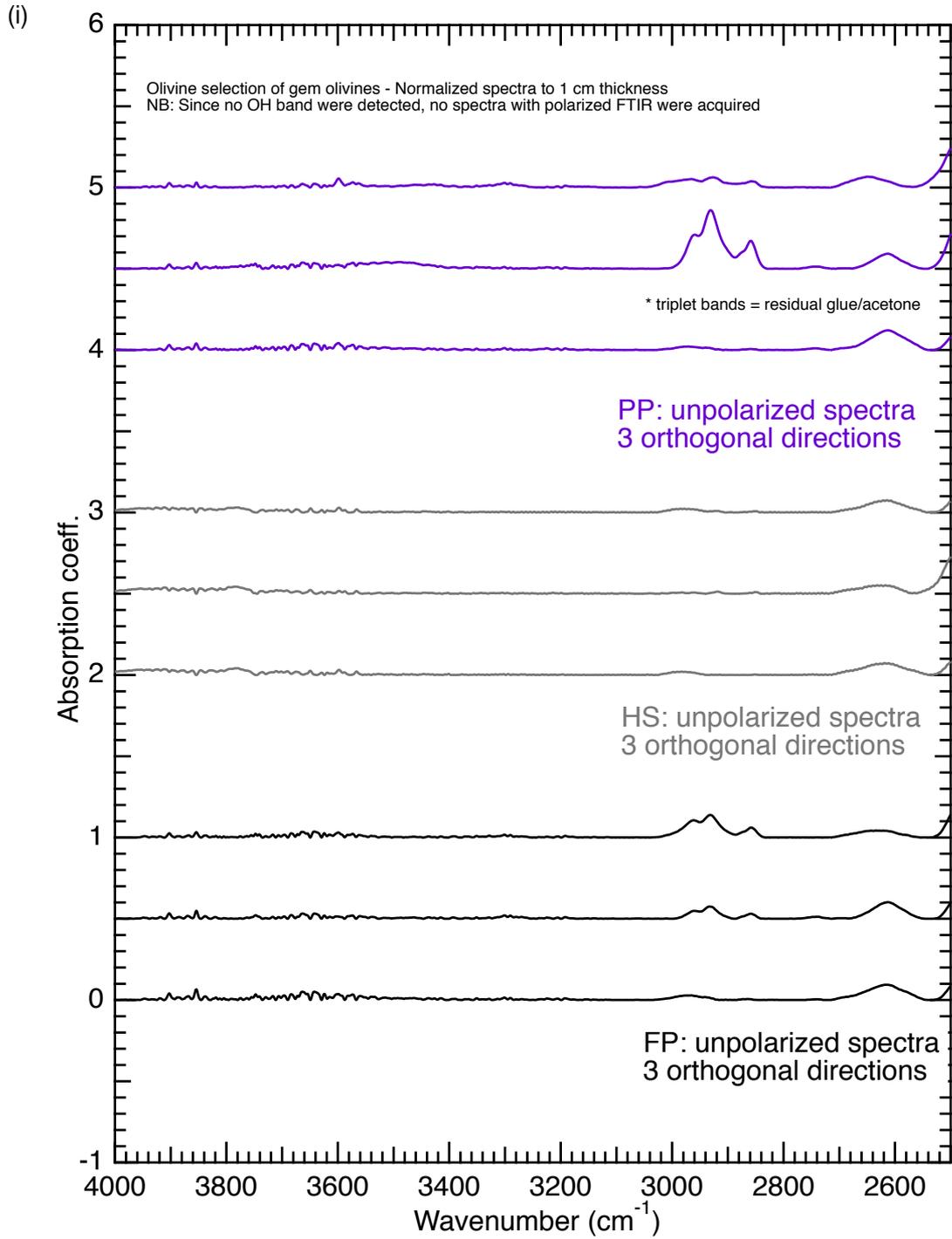


Fig. S3. Integrated absorbance distributions across (a) SAS20 and (b) NW1 as representative of the homogeneous distributions observed across all olivine specimens except Pa3.

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Fig. S2

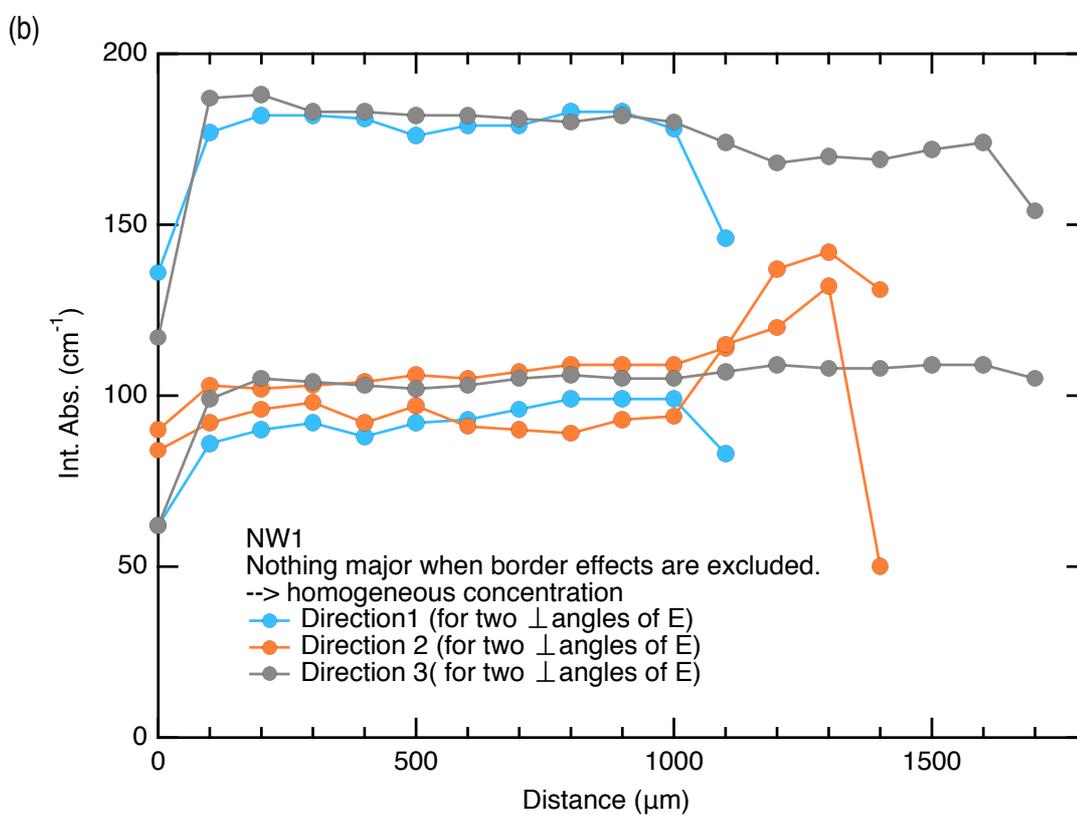
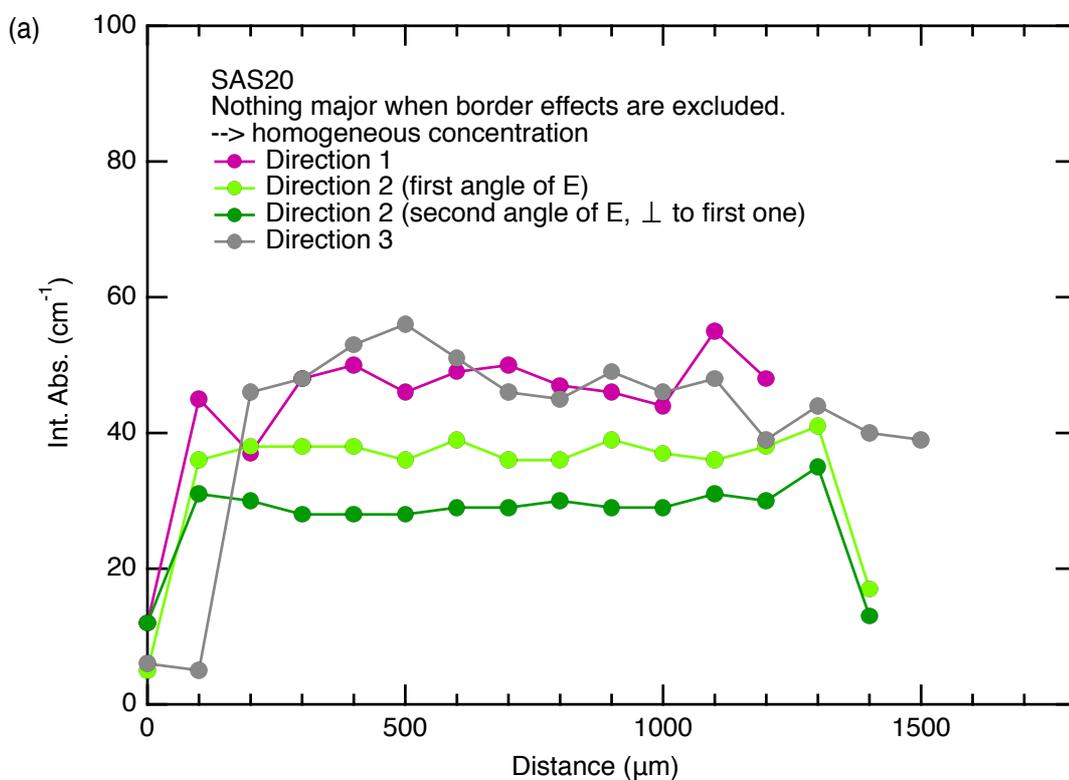
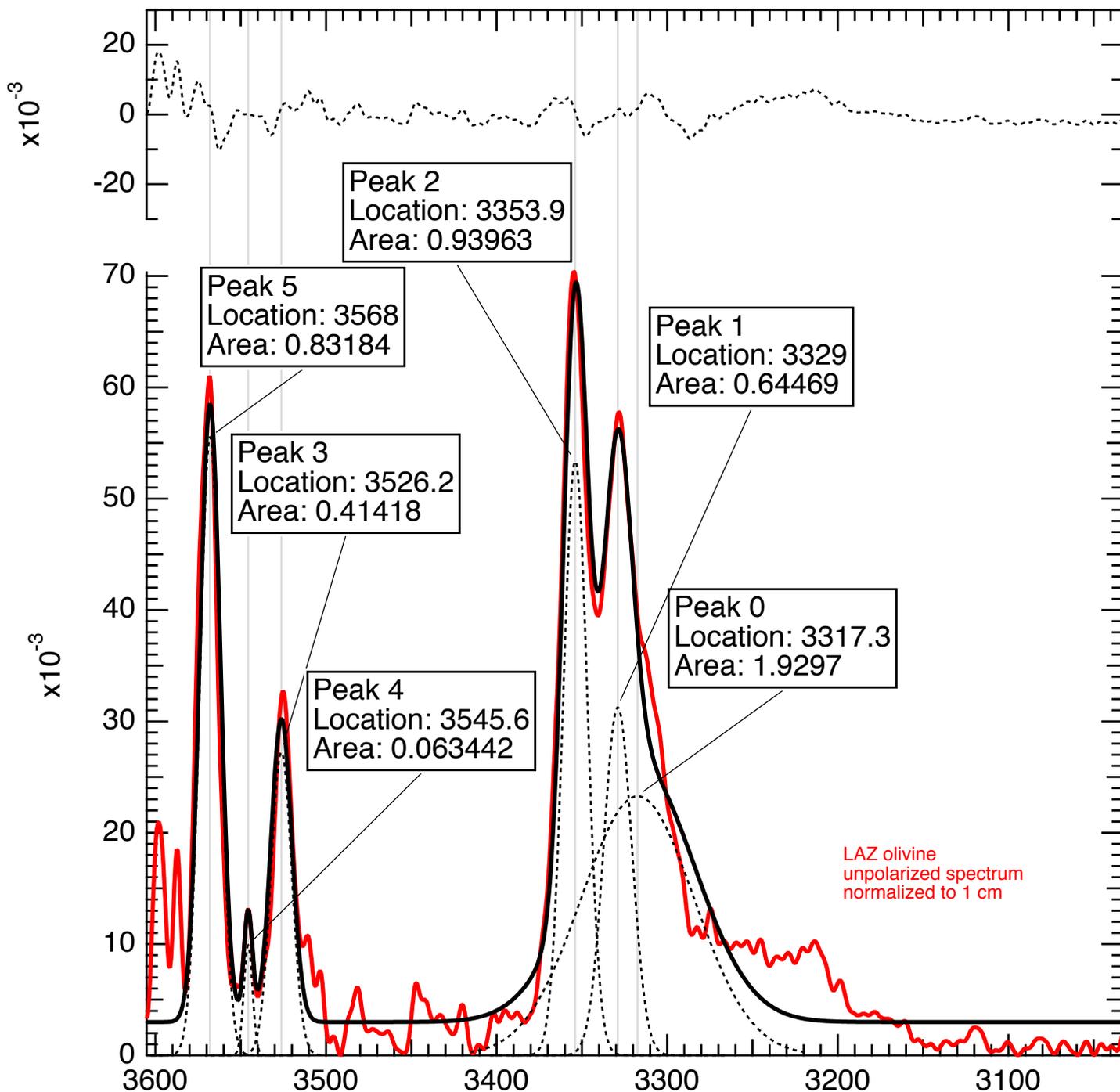
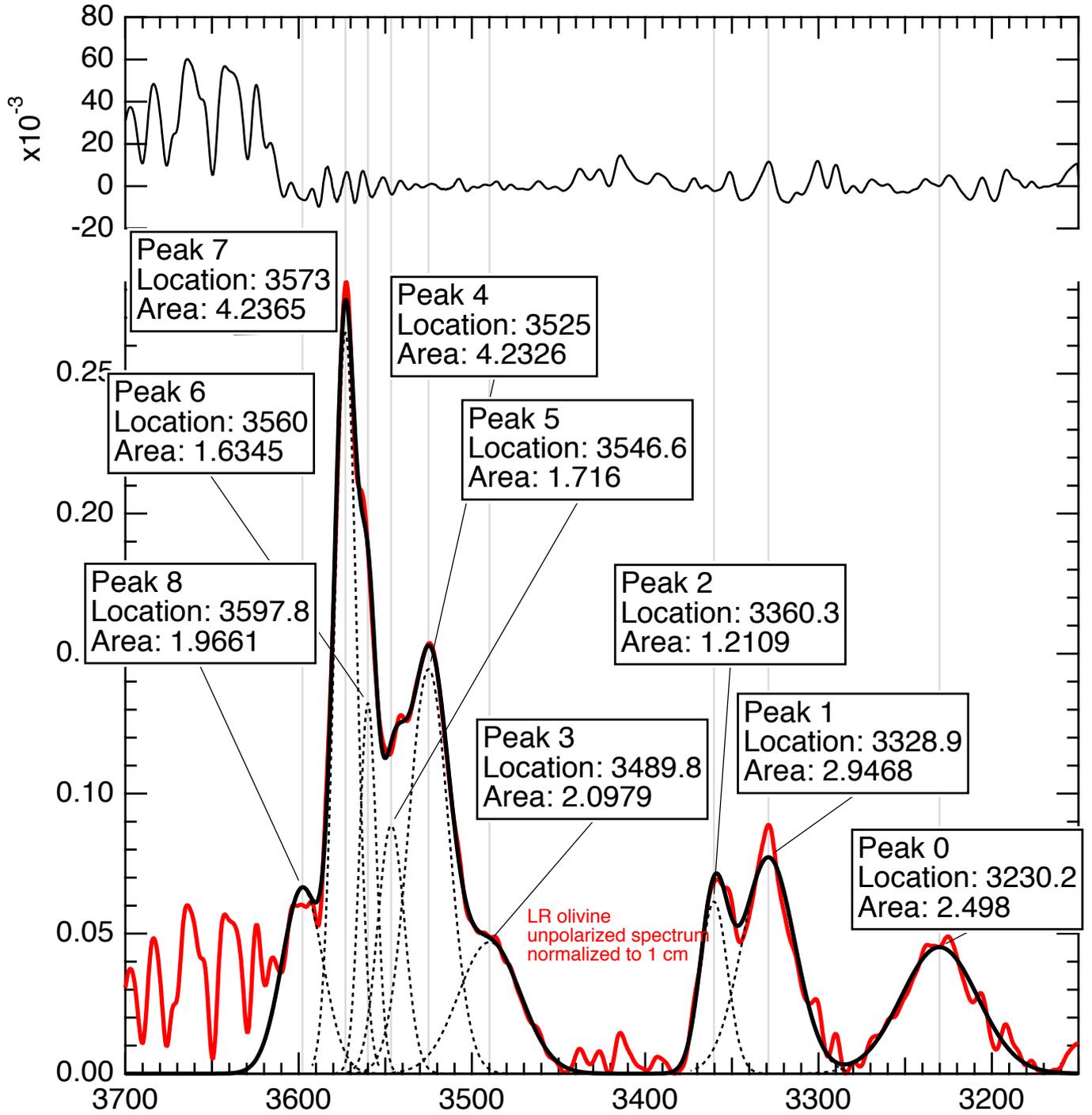


Fig. S4. Deconvolution details for the samples LR, LAZ, PA3, SAS20, SAS41, performed with the multipeak fitting package of IGOR PRO™ (<https://www.wavemetrics.com/products/igorpro>).

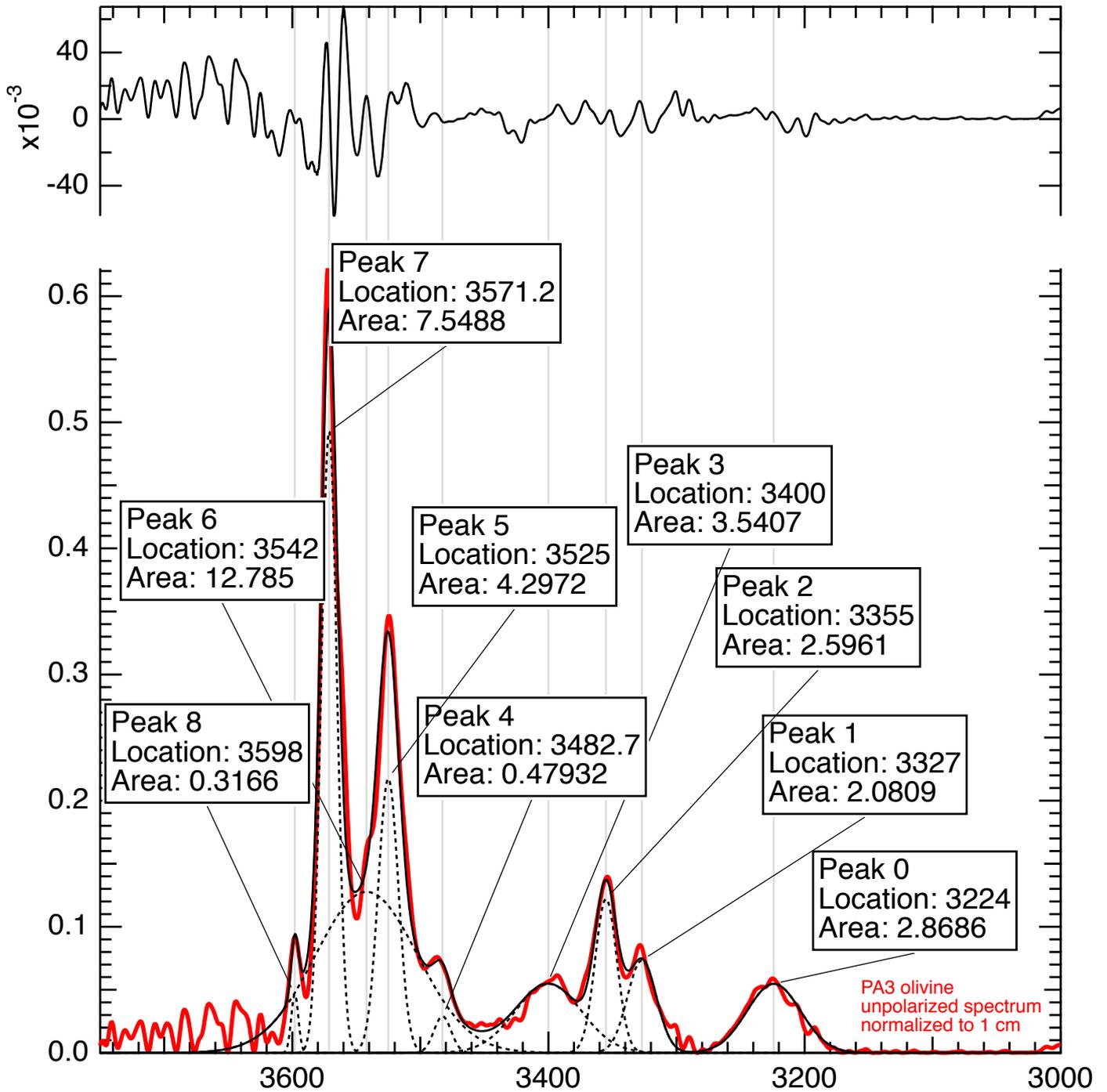
Deconvolution LAZ



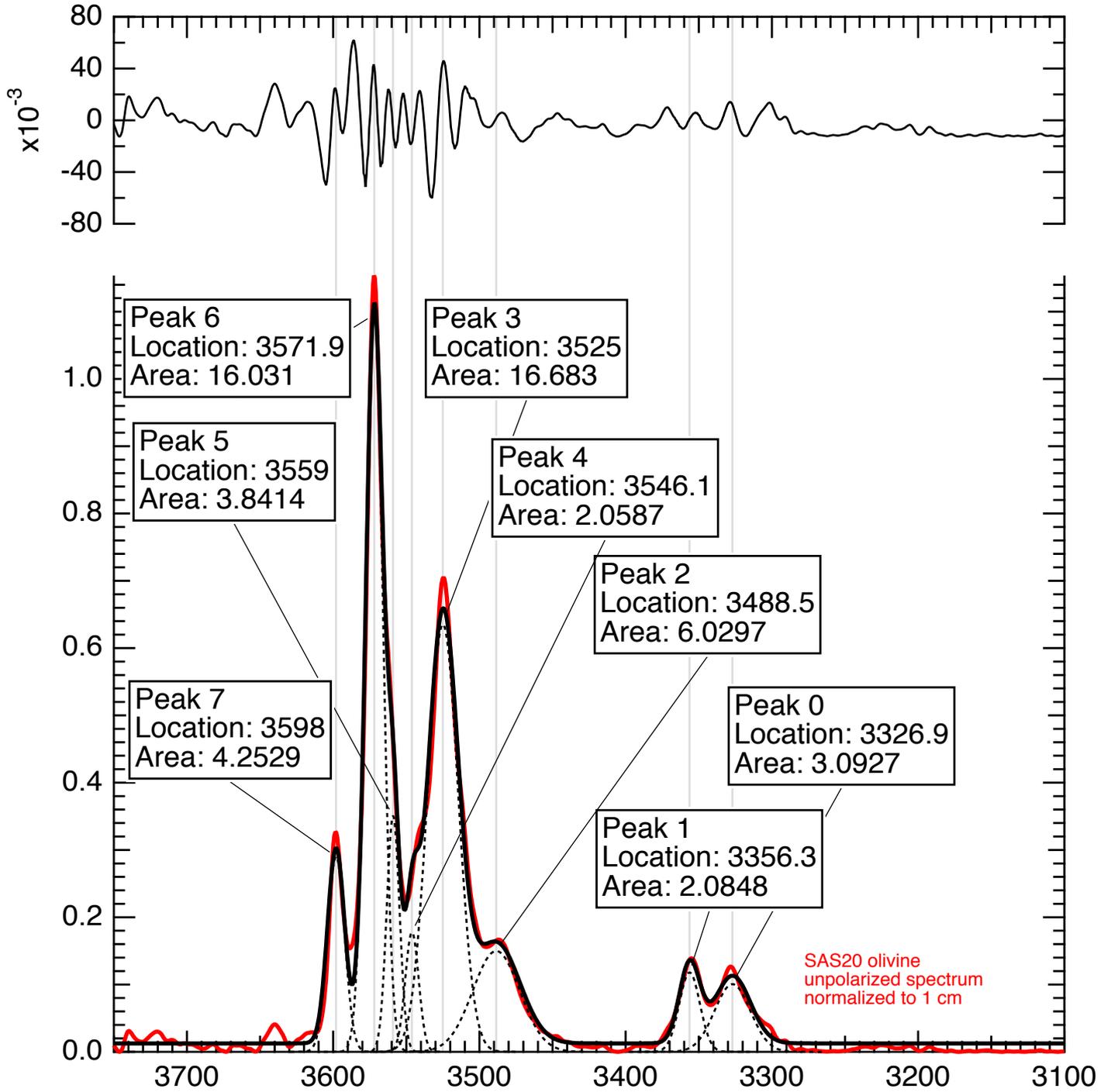
Deconvolution LR



Deconvolution PA3



Deconvolution SAS20



Deconvolution SAS41

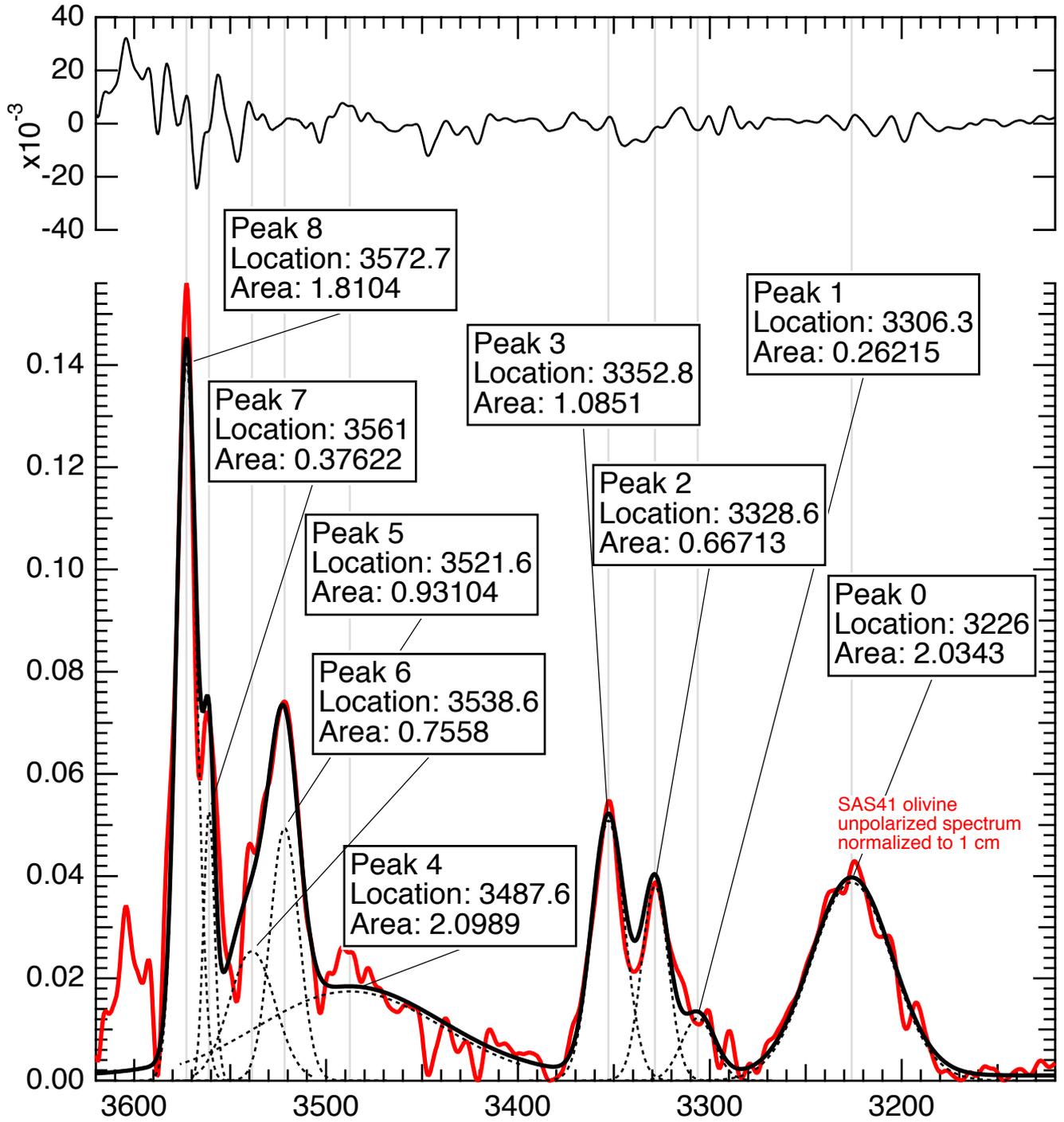


Fig. S5. Variations of Ni content (at. ppm) as a function of forsterite content ($\text{Fo}\% = 100 \times \text{Mg}/(\text{Mg}+\text{Fe})$) in the olivines studied herein and in previous studies: garnet peridotites (Peslier et al., 2010, 2012), spinel-bearing peridotites (O'Reilly et al., 1997; Satsukawa et al., 2017), olivine phenocrysts from Aeolian island arc lavas (Zamboni et al., 2017; *NB*, the field of arc lavas extends down to 200 ppm Ni and $\text{Fo}\% = 60$), olivine in various types of troctolites (Basch et al., 2018), and MORBs, OIBs (Hawaii), and Komatiites (Sobolev et al., 2007).

Demouchy and Alard, Fig. S5

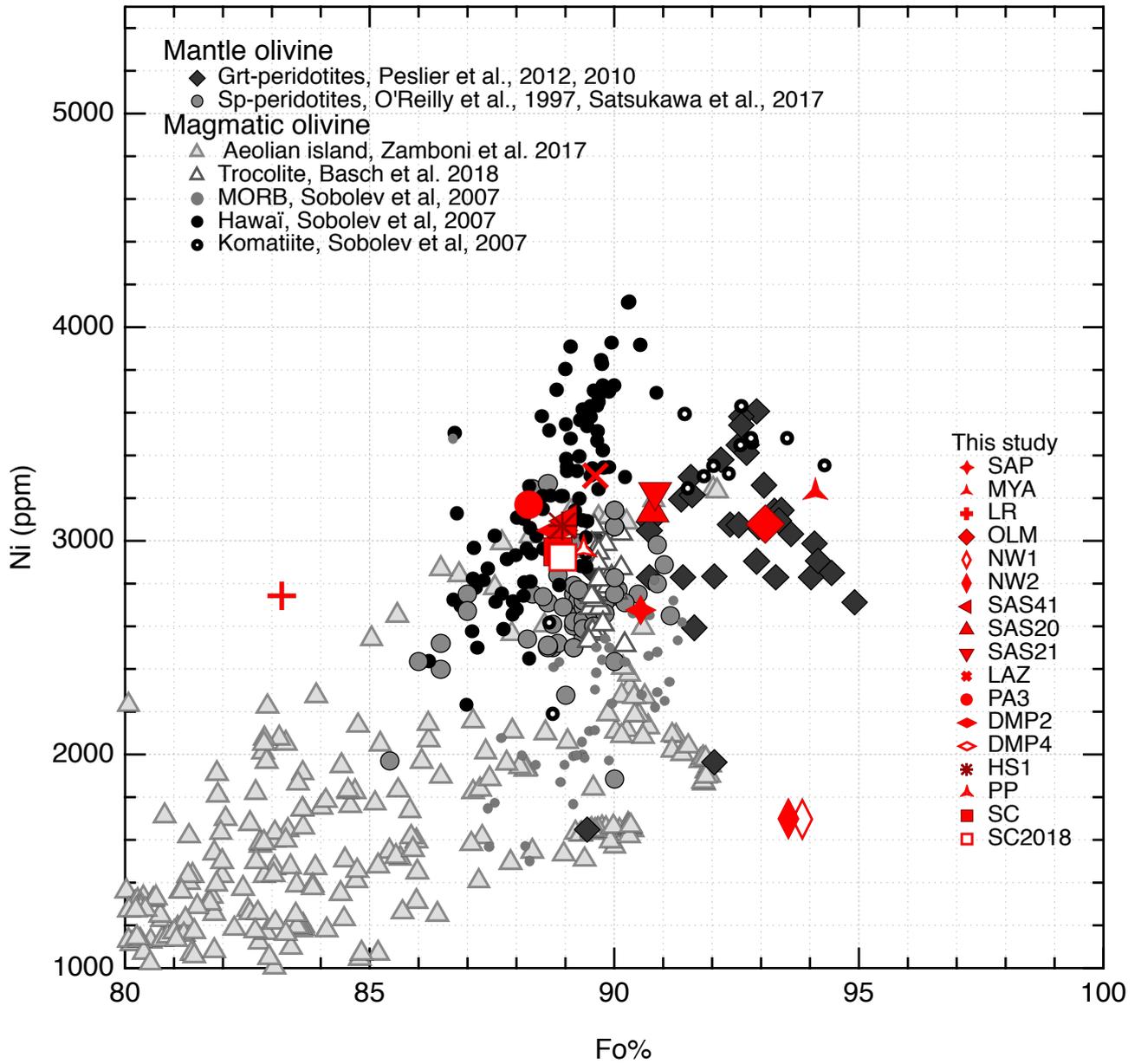


Fig. S6. Selected plots of trace element as a function of trace element concentration in micromole/g (B vs Li; Ti vs Cr/Na; Cr vs B; B vs H).

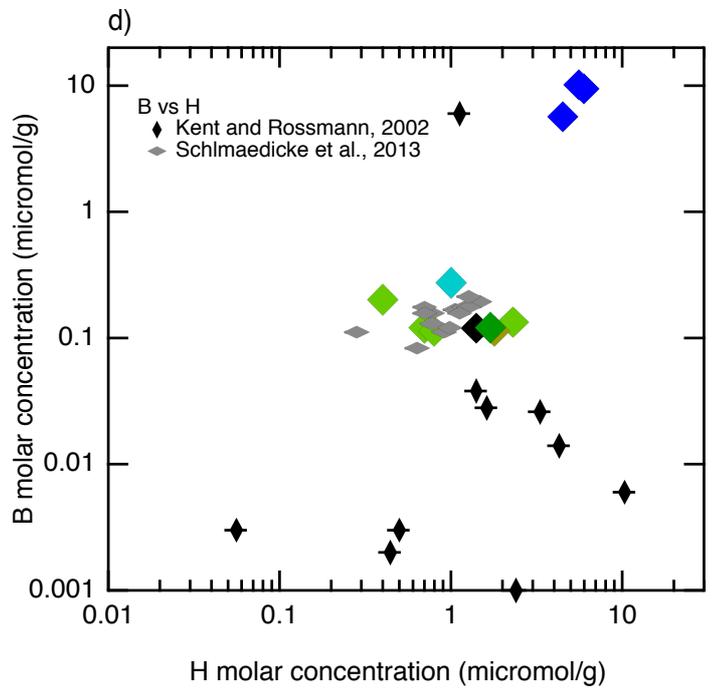
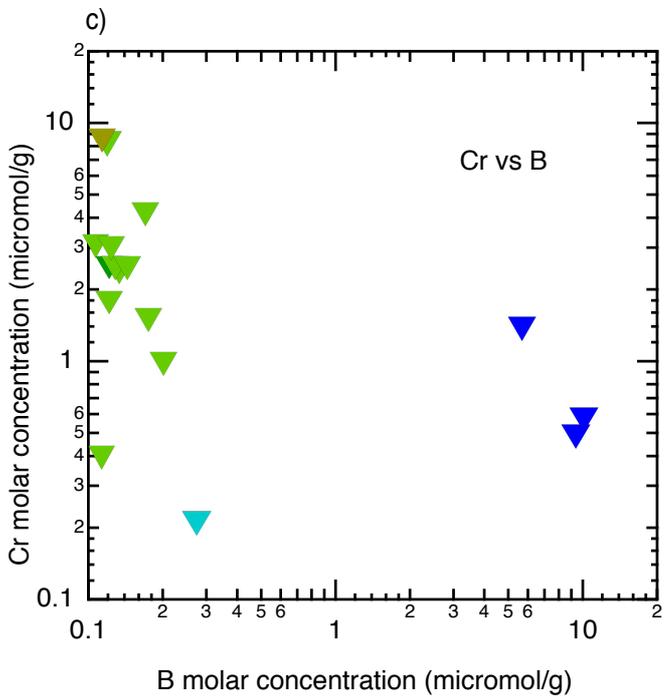
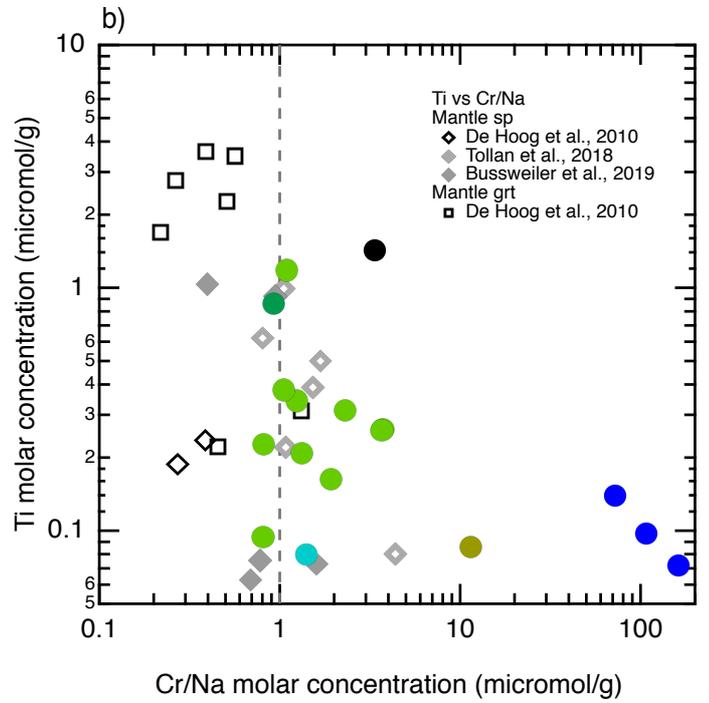
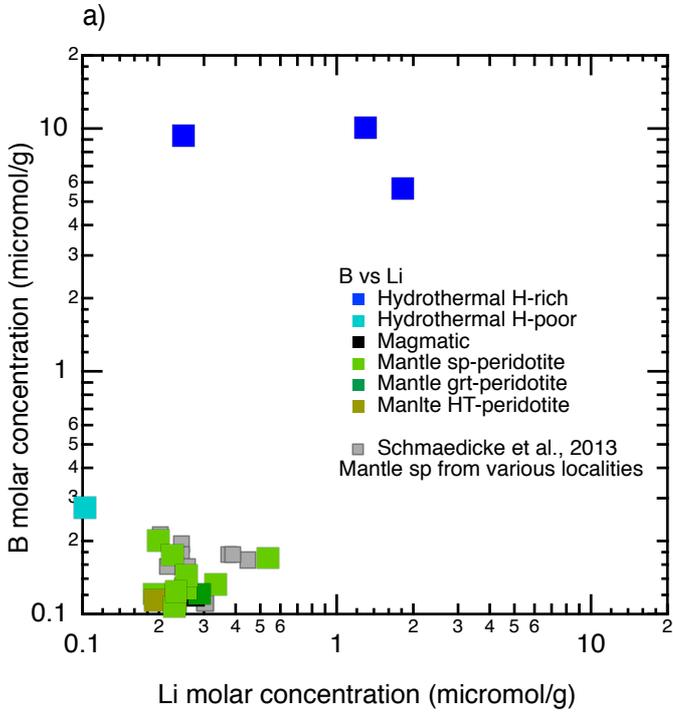


Fig. S7. Selected plots of trace element as a function of trace element concentration in micromole/g (Ti vs V; Cr vs V; Cr vs Al; Li vs B).

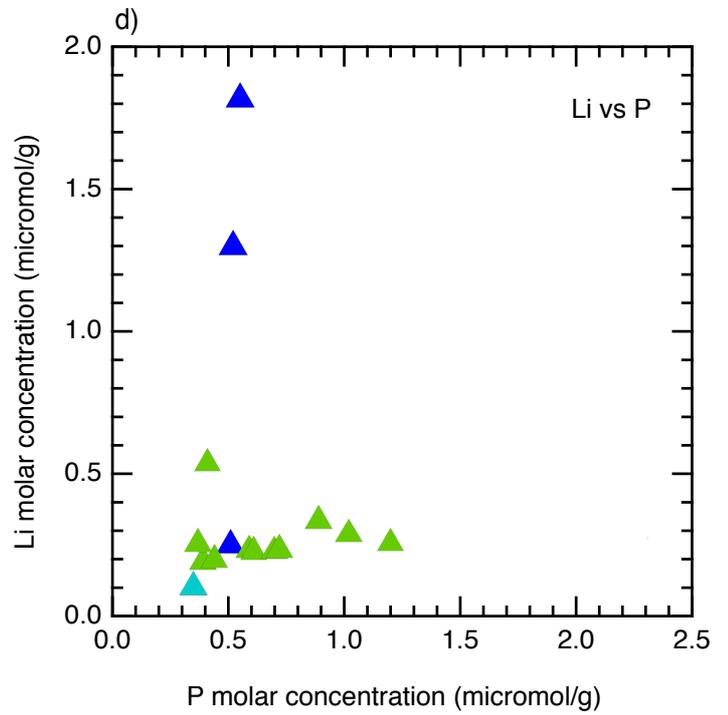
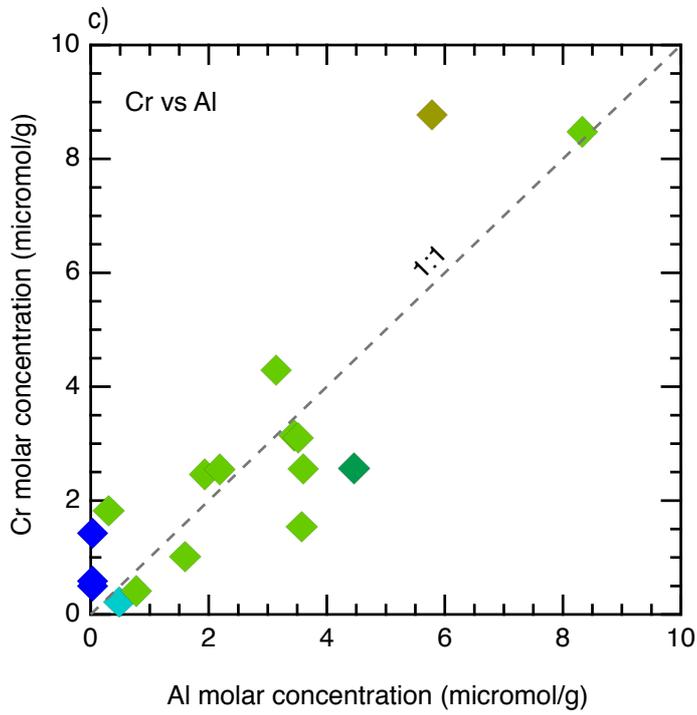
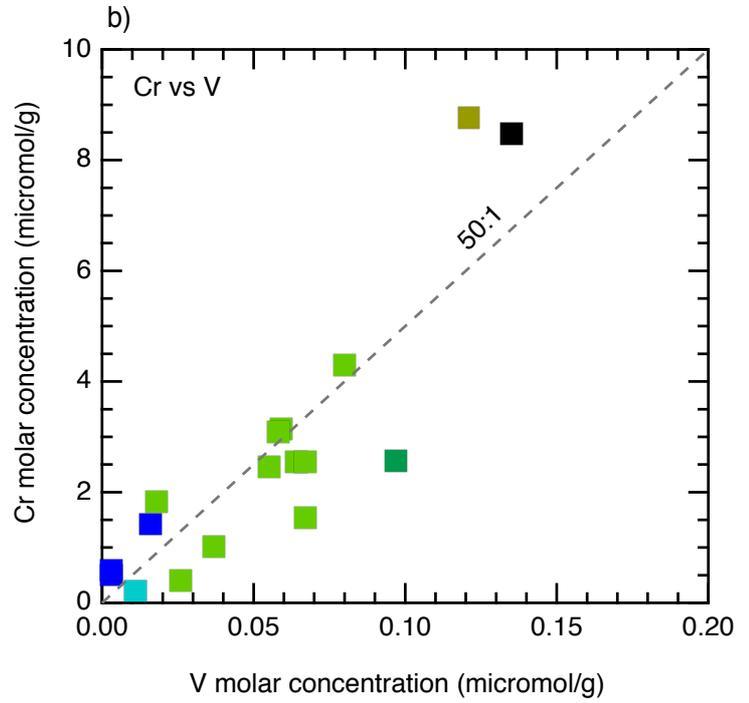
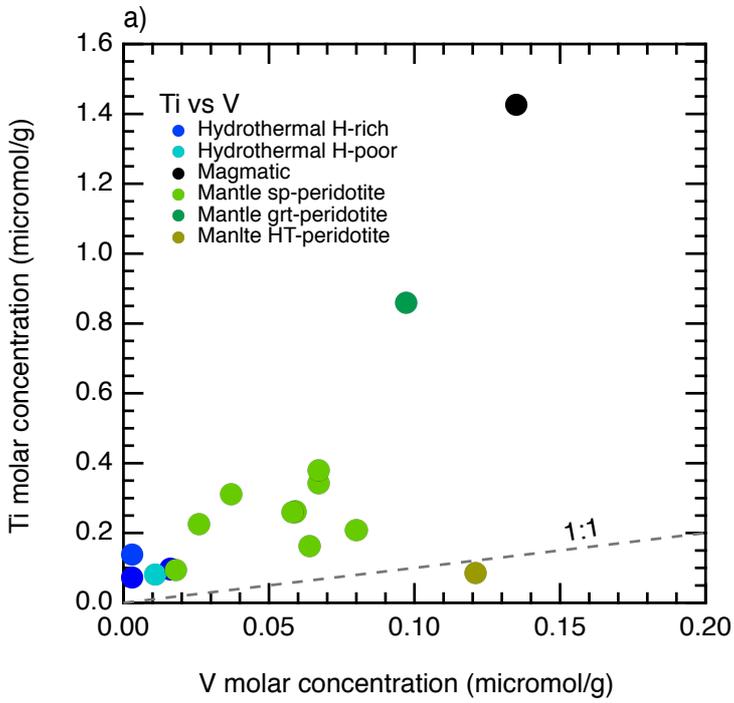


Fig. S8. Sum of mono-, di-, tri-, tetra and penta-valent elements as a function of hydrogen concentration in ppm by weight.

Demouchy and Alard
 Fig. S8 Revised

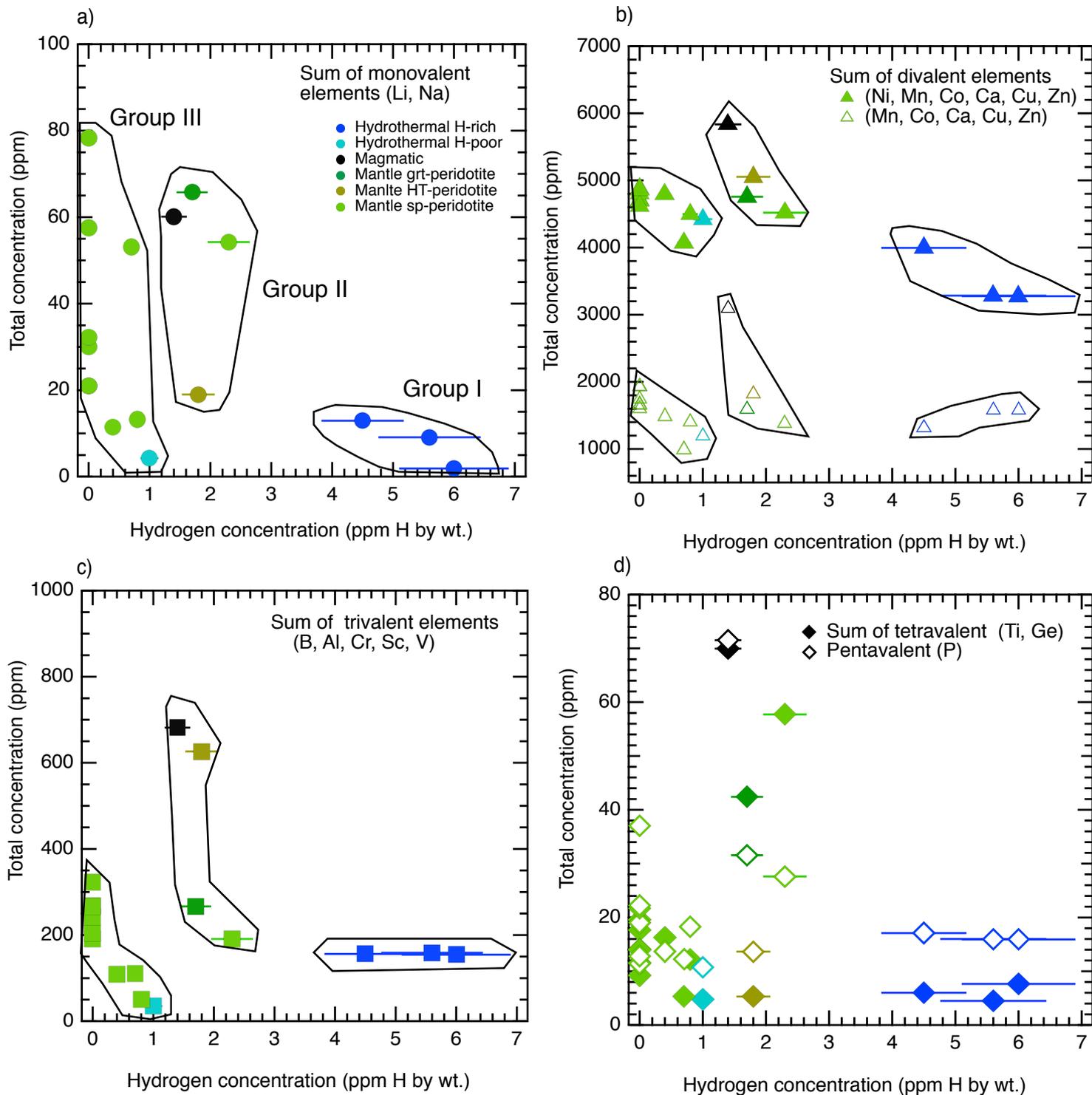


Fig. S9. (a) Sum of trivalent elements vs. sum of the monovalent elements; (b) Sum of trivalent elements vs. sum of the tetravalent elements; (c) Sum of tetravalent elements vs. sum of the monovalent elements; (d) Sum of pentavalent elements vs. sum of the monovalent elements.

Demouchy and Alard, Fig. S9

