1 **Revision 1:**

2 **Olivine from spinel peridotite xenoliths: Hydroxyl incorporation and mineral**

3 **composition**

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6 Esther Schmädicke[1*], Jürgen Gose[1], Gudrun Witt-Eickschen[2], and Helene Brätz[1]

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8 1: Universität Erlangen-Nürnberg, Geozentrum Nordbayern, Schlossgarten 5a, D-91054

9 Erlangen, Germany

10 2: Universität Köln, Institut für Geologie und Mineralogie, Zülpicher Str. 49a, 50674 Köln

11

12 * corresponding author; e-mail: esther@geol.uni-erlangen.de

13

14 **ABSTRACT**

15

16 Traces of water in mantle minerals strongly influence mantle melting and viscosity

17 which, in turn, govern large-scale processes like mantle convection, plate tectonics and

18 the stabilization of cratons. A major problem in estimating the mantle's water budget from

19 xenoliths arises from decompression-induced water loss during uplift. Mantle-derived

20 xenoliths have been investigated with respect to water from numerous occurrences

21 worldwide. However, little is known about water in the mantle beneath most parts of

22 Europe and Asia. This study presents water contents for mantle olivine from Germany,

23 Austria, Mongolia and Nigeria and suggests a possibility to assess water loss. It also

24 addresses the question whether or not water contents are related to olivine composition

25 and/or the presence of coexisting amphibole.

26   The highest water concentrations are present in olivine from the Eifel, Germany

27   (up to 21 ppm H_2O) whereas the Fichtelgebirge xenoliths, Germany, reveal the lowest

28   contents (<1 ppm). All water-bearing olivines show three dominant infrared absorption

29   bands: bands at 3572, 3525 and 3560 cm^{-1} and weaker bands at 3485, 3542 and 3597

30   cm^{-1}. The peaks at 3572 and 3525 cm^{-1} are ascribed to Ti related substitutions of H.

31   Additional peaks, related to H substitutions involving trivalent cations, occur in the 3300-

32   3400 cm^{-1} range. However, their intensity does not correlate with the content of trivalent

33   cations. The olivines show a pronounced correlation of Al + Cr and Ca implying that

34   incorporation of Al and Cr is governed by pressure and temperature and primarily

35   attributed to Tschermak's substitution. This study confirms that a coupled substitution

36   involving Ti is the most important mode of water storage in shallow upper mantle olivine.

37   The Ti content and the fraction of water bound to 'Ti defects' are related and support the

38   substitution model $Ti^{4+} + 2H^+ = Mg^{2+} + Si^{4+}$. Hence, the Ti content is useful to estimate

39   the maximum amount of water incorporated by this substitution – providing a tool to

40   approximate the degree of water loss. Five of the investigated olivines provide evidence

41   for no or very little water loss. Their water content of 16-21 ppm is presumably typical for

42   the depleted uppermost mantle. Twelve samples with <1-15 ppm may have lost from 36

43   to >80 % of their original water. Olivine from amphibole-bearing spinel peridotite has

44   relatively low water contents as well as low amounts of Ca, Al, Cr, Ti, and V. Particularly

45   low Ca, Al and Cr contents suggest fluid infiltration, amphibole formation and re-

46   equilibration of the whole assemblage at comparably low pressure and/or temperature

47   and may explain the low water content of olivine. Infrared spectra with dominant peaks in

48   the 3200-3300 cm^{-1} range (spectrum type E) are confined to olivine from amphibole-

49   bearing peridotite.

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51   Keywords: water content, nominally anhydrous minerals, olivine, spinel peridotite, trace

52   elements

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INTRODUCTION

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58   Water, or more precisely hydrogen, is present in the Earth's mantle as structural OH

59   groups in nominally anhydrous minerals such as olivine and pyroxene (e.g., Miller et al.

60   1987; Bell and Rossman 1992). Trace concentrations of water in mantle minerals have

61   significant influence on physical properties, melting behavior, mantle convection, plate

62   tectonics and the stabilization of cratonic roots (e.g., Karato 1990; Thompson 1992;

63   Hirose and Kawamoto 1995; Hirth and Kohlstedt 1996; Asimow and Langmuir 2003;

64   Peslier et al. 2010; Green et al. 2010). It has been shown that the water storage capacity

65   of mantle minerals is significant and depends on pressure, temperature, and mineral

66   composition (e.g., Kohlstedt et al. 1996; Rauch and Keppler 2002; Stalder 2004; Zhao et

67   al. 2004; Hirschmann et al. 2005). Olivine, as the most abundant mineral in the upper

68   mantle, has been investigated with respect to water concentration and possible

69   substitution mechanisms (e.g., Beran and Putnis 1983; Freund and Oberheuser 1986;

70   Miller et al. 1987; Bai and Kohlstedt 1993; Sykes et al. 1994; Libowitzky and Beran 1995;

71   Khisina and Wirth 2002; Gose et al. 2010) for more than three decades. The most

72   commonly applied analytical method, infrared (IR) spectroscopy, is very sensitive to

73   detect trace amounts of water and simultaneously provides information on substitution

74   mechanisms.

75

76   Several experimental studies were conducted to investigate the water storage capacity of

77   olivine as a function of pressure, temperature and chemical environment (e.g., Bai and

78   Kohlstedt 1993; Kohlstedt et al. 1996; Zhao et al. 2004; Grant et al. 2006, 2007;

79   Mosenfelder et al. 2006; Smyth et al. 2006; Bali et al. 2008). The experiments have

80   shown that water solubility in olivine is pressure-enhanced. The temperature effect on

81   water solubility, however, is controversial and may vary with pressure. For pressures of

82   2.5 and 3.0 GPa, water solubility increases with temperature (Zhao et al. 2004; Bali et al.

83   2008), whereas at 2.0 GPa, temperature has no visible influence on water content in

84   olivine (Grant et al. 2006). Further experiments with different olivine compositions,

85   including a variety of trace elements, were directed to identify possible substitution

86   mechanisms that enable the incorporation of water in the olivine structure (e.g., Bai and

87   Kohlstedt 1993; Lemaire et al. 2004; Berry et al. 2005; Berry et al. 2007b). This

88   information is important to interpret the infrared absorption spectra of natural samples.

89   More than 20 absorption bands were identified in natural olivine (Beran and Libowitzky

90   2006; and references therein). A single crystal may contain more than 10 different bands

91   in the infrared absorption spectrum caused by intrinsic water in the olivine structure (e.g.,

92   Khisina et al. 2001; Koch-Müller et al. 2006). For a review and further references see

93   Beran and Libowitzky (2006).

94

95   Another field of research focuses on the quantification of water in natural olivine

96   samples, predominantly those of mantle heritage. These studies provide information on

97   actual water contents in the upper mantle. Naturally, measured contents comprise the

98   whole range from zero up to the maximum water storage capacity. Data were collected

99   for mantle samples from most parts of the world. The focus has been on peridotite

100   xenoliths; the majority of which represents the sub-continental mantle and includes

101   samples from cratons and non-cratonic areas (e.g., Miller et al. 1987; Bell and Rossman

102   1992; Kurosawa et al. 1997; Bell et al. 2004; Demouchy et al. 2006; Yang et al. 2008;

103   Soustelle et al. 2010). Fewer data are available for massive-type peridotite and

104   pyroxenite (e.g., Hermann et al. 2007; Gose et al. 2008) and even less data for sub-

105   oceanic peridotite (Gose et al. 2009; Schmädicke et al. 2011).

106

107   Low water contents were identified as a characteristic feature of the cratonic mantle, and

108   were interpreted as a probable pre-condition for the stabilization of cratons (Peslier et al.

109   2010). Samples from non-cratonic areas (New Mexico, Washington State; e.g., Bell and

110   Rossman 1992; Peslier and Luhr 2006) may also be water-poor. However, it has been

111   shown that these contents need not reflect the original mantle contents but were

112   probably caused by water loss due to uplift and decompression (Peslier and Luhr 2006)

113   favored by fast diffusion of hydrogen in olivine (Demouchy and Mackwell 2006).

114

115   More data on olivine water contents are needed for non-cratonic mantle xenoliths. Data

116   are available for various parts of the world, including Africa, North America (Bell and

117   Rossman 1992; Peslier and Luhr 2006) and Asia-Pacific (Kurosawa et al. 1997; Yang et

118   al. 2008; Soustelle et al. 2010). Comparably little, however, is known from European

119   xenolith occurrences. Falus et al. (2008) focused on occurrences in Eastern Europe. In

120   the present study we concentrate on xenoliths from Central Europe, specifically from

121   Germany, and include further samples from other occurrences. We present analytical

122   data on water contents and concentrations of major and trace elements in olivine. The

123   aim of the investigation is to address the following questions: 1. What are the typical

124   water contents in olivine from non-cratonic spinel peridotite xenoliths in Central Europe

125   compared to other parts of the world? 2. Is there a relation between water content and

126   olivine composition, trace elements included? 3. Is the infrared absorption spectrum

127   related to the trace element content in olivine? 4. Is there a difference in water content

128   and/or spectrum type between amphibole-bearing and amphibole-free peridotite

129   xenoliths? 5. Are there any signs of water loss and, if so, can the original contents be

130   estimated?

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132

133   **SAMPLES AND METHODS**

134

135   All olivine samples are derived from spinel peridotites occurring as xenoliths in alkali

136   basalt. The majority of samples (12) stem from the Eifel and the Fichtelgebirge in the

137   western and southeastern part of Germany, respectively. Further samples from Mongolia

138   (3 samples), Austria and Nigeria (1 sample each) were included for comparison. A

139   sample list is given in Table 1. Most spinel peridotites are characterized by the four-

140   phase assemblage olivine, orthopyroxene, clinopyroxene, and spinel. Four samples,

141   three from the Eifel area and the one from Austria, contain additional calcic amphibole

142   (Table 1). The olivine grains of the investigated samples have typical grain diameters of

143   1-3 mm; only the sample from Nigeria has a larger grain size of 10 mm.

144

145   The major element composition of olivine was determined with a JEOL 8200 electron

146   microprobe, equipped with five wavelength dispersive spectrometers, including a high-

147   resolution spectrometer and operating at 15 kV and 15 nA. A counting time between 20

148   and 40 seconds was applied for major and most minor elements; only Ca was measured

149   for 60 seconds. Silicate and oxide standards were used for the calibration. The analytical

150   error of the results displayed in Table 2 is ≤ 1 % (relative). At least 10 spot analyses were

151   obtained for each sample, measured on different sites to unravel possible compositional

152   zoning.

153

154   The trace element composition was obtained by LA-Q-ICP-MS using an UP193FXesi®

155   laser ablation unit coupled to an Agilent 7500i quadrupole inductively- coupled plasma

156   mass spectrometer, tuned for maximum sensitivity by ThO/Th <0.5 %. Ar was used as

157   plasma and cooling gas (14.9 L/min), auxiliary gas (0.9 L/min) and carrier gas (1.1 L/min)

158   while He was utilized as second carrier gas (0.65 L/min). Each olivine was measured 4

159   times at different sites, including core and rim areas. Spot diameter and repetition rate

160   were 25 µm and 20 Hz, respectively, by applying an irradiance of 0.56 GW/cm^2 and a

161   fluence of 2.8 J/cm^2. The background and mineral ablation times were 20 and 25

162   seconds, respectively. External calibration was performed on the NIST SRM 612

163   standard applying linear fit, and SiO_2 determined by microprobe was used as internal

164   standard. Data evaluation was carried out with GLITTER (van Achterbergh et al. 2000).

165   Microanalytical reference material BCR-2G (USGS) was used as secondary standard to

166   check for reproducibility (mostly <5 %) and accuracy (mostly <8 %) of the method.

167

168   The water content of olivine was determined by IR spectroscopy using a Bruker Tensor

169   27 Fourier transform IR spectrometer equipped with a Hyperion 3000 microscope and an

170   MCT detector. For the FTIR analysis, clear and transparent crystal areas free of

171   inclusions, cracks and alteration products were carefully selected. Spectra were collected

172   in a transmittance mode, using a square aperture of 40 x 40 to 60 x 60 µm^2 to restrict the

173   lateral size of the probed spatial regions.

174

175   The samples were first investigated with non-polarized IR radiation (qualitative analysis)

176   using doubly polished and self-supporting rock slices with a thickness of 0.3 to 1.5 mm,

177   depending on crystal quality and size. These qualitative analyses were used to

178   investigate a relatively large number of grains for the presence (or absence) of water and

179   also to recognize possible zonation patterns in terms of water content or spectrum type

180   by comparing analyses from core and rim areas.

181

182   Quantitative analysis of water in an anisotropic mineral is possible by measurements

183   either using polarized IR radiation in different directions of a single crystal (e.g.,

184   Libowitzky and Rossman 1996) or utilizing non-polarized IR radiation on multiple

185   randomly oriented grains (e.g., Kovács et al. 2008; Withers 2013). The first approach has

186   been preferred in geological science, whereas the second approach is useful if crystal

187   size is not large enough to prepare oriented slices (Kovács et al. 2008). The samples

188   investigated in this study have grain sizes that are large enough to prepare defined slices

189   of single crystals. In the case of a randomly oriented single crystal, measurements in

190   three orthogonal directions and two polarizer positions (0 and 90°, equivalent to

191   maximum and minimum absorption) are necessary, resulting in six spectra per sample

192   (Libowitzky and Rossman 1996). If it is possible to prepare oriented slices, two

193   orthogonal sections each parallel to two indicatrix axes are needed in order to

194   accomplish the measurements along the three indicatrix axes (Libowitzky and Rossman

195   1996). Thus, representative single olivine crystals were extracted from the slices by

196   cutting with a wire-saw and prepared as cuboid bodies, polished on all six planar sides.

197   The typical size of the bodies is 1 mm^3 but some specimens are as small as 0.03 mm^3

198   and the largest one has a size of c. 10 mm^3. These specimens were measured with

199   polarized IR radiation, using a gold wire polarizer, in the required directions resulting in

200   three or six spectra per sample, according to crystal orientation. The spectra were

201   obtained by averaging over 128 scans in the wavenumber range 2000-4000 cm^{-1} with an

202   instrumental resolution of 2 cm^{-1}. Water contents were calculated by summing the

203   average data from the three directions as described by Libowitzky and Rossman (1996),

204   applying the mineral-specific molar absorption coefficient of Bell et al. (2003). The

205   integral absorbance was determined by fitting the spectra between 3000 and 3620 cm^{-1}

206   using a polynomial baseline correction. The peak fit was obtained by a combination of

207   Lorentzian and Gaussian functions using a varied weight coefficient for all samples.

208   Figure 1 shows an example of a de-convoluted spectrum. The uncertainty of the

209   calculated water contents given in Table 3 is ≤ 10 %. Water attributed to Ti related

210   defects (see Table 3) was inferred from the peak areas of the two diagnostic peaks at

211   peaks at 3525 and 3572 cm^{-1}. For more information on the method and sample

212   preparation see Gose et al. (2009) and Schmädicke et al. (2011).

213

214

RESULTS

216

Mineral composition

218

219   All olivines are unzoned and have similar major element compositions but can differ in

220   minor and trace element concentrations. All samples have Mg# (= Mg/(Mg+Fe); Table 2)

221   in the range of 0.89-0.92. The typical Mg# of most samples is 0.91. The samples from

222   Mongolia are characterized by lower values of 0.89-0.90, and two samples from the Eifel

223   have Mg# of 0.92. The minor elements Mn and Ni and the trace elements Co, P, and Ge

224   have rather uniform concentrations in all samples (Table 2). The NiO and MnO contents

225   cluster in the range of 0.30-0.40 and 0.10-0.18 wt.%, respectively. The Co and P

226   contents comprise a range of 145-167 ppm and 66-100 ppm, respectively. The contents

227   of Li (1.4-3.1 ppm), B (0.9-2.3 ppm) and Sc (2.1-4.4 ppm) show moderate variability.

228   Concentrations of Be, and rare earth elements are below the detection limit. Fluorine

229   contents are below the detection limit of the electron microprobe and cannot be

230   measured by ICP-MS. If F is incorporated by the coupled substitution $B(OH,F)Si_{-1}O_{-1}$

231   (Sykes et al. 1994), the F contents should be <2.3 ppm in the investigated olivines.

232

233   Pronounced compositional variations are shown by the elements Ti, Cr, Al, Ca, and V (in

234   decreasing order). Aluminum ranges from 56 to 362 ppm; the whole compositional range

235   is present in the Eifel samples. The four samples in which olivine coexists with amphibole

236   are characterized by comparably low Al contents of ≤109 ppm (E-194: 109 ppm, E-211:

237 56 ppm, E-213: 64 ppm, Kapf: 87 ppm). The Ca contents of all samples are in the range

238 of 290-1000 ppm. Again, the four amphibole-bearing samples reveal relatively low Ca

239 contents of ≤510 ppm. The Cr contents vary in the range of 28-362 ppm, and are ≤139

240 ppm in the amphibole-bearing samples. Vanadium ranges from 2.0 to 7.2 ppm (≤2.8 ppm

241 in amphibole-bearing samples). Titanium shows the strongest compositional variation in

242 the sample set, ranging from 4 to 66 ppm. The Ti contents of the Eifel samples are in the

243 range of 4-50 ppm, whereas samples from Fichtelgebirge (4-12 ppm) and Mongolia (22-

244 39 ppm) show lower variability. Olivine from amphibole-bearing peridotites is

245 characterized by Ti contents of 4-26 ppm.

246

247 The olivine samples reveal a pronounced positive correlation between Ca and the

248 content of Al + Cr, with a coefficient of determination R^2 of 0.98 (Fig. 2a). A similar

249 positive correlation is found in plots of Ca versus Al (R^2 = 0.92; Fig. 2b) and of Ca versus

250 Cr (not shown), respectively. Moreover, the contents of Ca and Sc are positively

251 correlated (R^2 = 0.85; Fig. 2c) as well as the contents of Al and Sc (not shown). A

252 correlation of Ti and V (Fig. 2d) or Ti and Al (not shown) is very poor to nonexistent (R^2 ≤

253 0.28).

254

255 **Infrared absorption patterns**

256

257 The infrared absorption spectra of most olivine samples reveal stretching bands caused

258 by structurally incorporated hydroxyl groups or 'water'. Exceptions are the three samples

259 from the Fichtelgebirge that are devoid of any detectable peaks in the infrared spectra.

260 All other samples possess at least six separate absorption bands. Considering the

261 spectra from all samples, 11 peaks can be distinguished. The main bands occur in the

262 wavenumber range from 3450 to 3650 cm^{-1} (Fig. 3). Additional peaks in the range of

263   3100-3400 cm^{-1} have weaker intensities. Peaks in the wavenumber range from 3450 to

264   3650 cm^{-1} have been referred to in the literature as ‚high frequency' or ‚group I' bands;

265   those in the 3100-3450 cm^{-1} range as ‚low frequency' or ‚group II' bands (Bai and

266   Kohlstedt 1993; Lemaire et al. 2004; Matveev et al. 2005). The high frequency peaks are

267   basically identical in all investigated samples. Differences in the absorption patterns are

268   restricted to the low frequency range and are the basis to distinguish the five types of

269   spectra A, B, C, D, and E (Fig. 3; Table 3). Spectrum E is restricted to olivine that

270   coexists with amphibole,

271

272   The IR absorption patterns reveal pronounced pleochroism. The strongest absorption

273   commonly occurs parallel to the crystallographic a-axis of olivine. Only the peaks at 3230

274   and 3328 cm^{-1} show the strongest absorption parallel c. The weakest absorption of all

275   peaks is observed parallel b.

276

277   The high frequency peaks show the following characteristics: The strongest peak in all

278   samples (in spectra taken parallel a) occurs at 3572 cm^{-1}. Further dominant peaks at

279   3525 (second strongest) and 3560 cm^{-1} (third strongest) and weaker peaks at 3485,

280   3542 and 3597 cm^{-1} are present in all spectra types. A very weak peak occurring around

281   3613-3615 cm^{-1} is found only in spectra B, D, and E.

282

283   The weak peaks at 3328 and 3356 cm^{-1} are present in the spectra types A, B, and C.

284   Furthermore, a broad asymmetric peak around 3230 cm^{-1} occurs in spectra A and E. In

285   spectrum C it is visible that this peak is split into two small peaks. This peak is strongly

286   pleochroitic with maximum absorption parallel c (Fig. 3). Another small peak at 3403 cm^{-}

287   ^{1} is only found in spectrum E.

288

289   **Band assignment**

290

291   The two strongest peaks at 3572 and 3525 cm^{-1} are present in almost every mantle

292   olivine (Miller et al. 1987). In olivine from spinel peridotite xenoliths, these peaks are the

293   most prominent ones in the IR absorption spectra and are correlated with the dominant

294   mode of water incorporation in the spinel peridotite facies. Laboratory experiments failed

295   to reproduce these peaks in synthetic olivine under relevant conditions (Matveev et al.

296   2001; Lemaire et al. 2004; Mosenfelder et al. 2006) except for experimental charges in

297   equilibrium with rutile (Berry et al. 2005; 2007a; Walker et al. 2007). These authors

298   suggested that the two bands are caused by Ti-related OH point defects rather than by

299   planar Ti-clinohumite defects, unless a further broad peak around 3400 cm^{-1} appears in

300   the spectrum. Such a peak is present only in spectrum type E, as displayed by the three

301   amphibole-bearing samples E-194, E-211, and E-213 from the Eifel (Fig. 3; Table 3). All

302   other samples lack the 3400 cm^{-1} band suggesting that water incorporation is

303   presumably dominated by Ti-point defects. A possible substitution mechanism involves

304   replacement of a divalent cation by Ti^{4+} on an octahedral site charge-balanced by

305   substitution of Si^{4+} by two protons on a tetrahedral site (Berry et al. 2005, 2007a; Walker

306   et al. 2007). Planar Ti-clinohumite defects seem to be restricted to amphibole-bearing

307   samples from the Eifel. However, the diagnostic peak at 3400 cm^{-1} is very small relative

308   to other peaks. Hence, planar Ti-clinohumite, if present at all, is only of minor

309   importance.

310

311   Other bands in the high frequency range of 3450 to 3650 cm^{-1} are presumably related to

312   Si vacancies in a tetrahedral site, each of which is charge-balanced by four protons

313   (Lemaire et al. 2004; Walker et al. 2007). This includes the relatively strong peak at 3560

314   cm^{-1} and the peaks at 3485, 3542, and 3597 cm^{-1} that are present in all samples and,

315   thus, in all five spectra types. An additional peak around 3613-3615 cm^{-1}, also ascribed

316   to Si vacancies (Gose et al. 2010), is present in two samples from the Eifel (spectrum

317   type B), in the three samples from Mongolia and in the Nigeria sample (all spectrum type

318   D).

319

320   The bands in the low-frequency range of 3100-3400 cm^{-1} are divided into two groups, (i)

321   3100-3300 and (ii) 3300-3400 cm^{-1} because they are presumably induced by two types

322   of substitutions (e.g., Kovács et al. 2010; and references therein). Peaks in the interval of

323   3100-3300 cm^{-1} are interpreted as Mg-site vacancies, ascribed to substitution of a

324   divalent cation (predominantly Mg) by two protons. Such peaks are most pronounced in

325   our spectra A and E, weak in spectra B and C, and absent in D (Fig. 3). These strongly

326   pleochroitic peaks show maximum absorption parallel to the c axis.

327

328   Peaks in the interval 3300-3400 cm^{-1} are related to substitutions involving trivalent

329   cations (e.g., Berry et al. 2005; Berry et al. 2007b; Grant et al. 2007). The mechanism by

330   which hydrogen is incorporated involves a coupled substitution in which two divalent

331   cations (e.g., Mg^{2+}) are replaced by H^+ and a trivalent cation, predominantly Al^{3+} or Fe^{3+}.

332   Moderately sized peaks in this range occur in spectra A, B, and E; spectrum C reveals

333   small peaks and spectrum D has no peaks in this range (Fig. 3).

334

335   **Water contents**

336

337   The investigated olivine samples are characterized by low water contents of ≤21 ppm

338   H_2O (Table 3). Traces of water are present in all samples, except of those from the

339   Fichtelgebirge where contents are below the detection limit (<1 ppm H_2O). The Eifel

340   samples show the highest water concentrations ranging between 10 and 21 ppm. The

341   water contents of the remaining samples, from Mongolia, Austria and Nigeria, are in the

342   range of 4-16 ppm H_2O. Differences between olivine cores and rims were not found. The

343   total water contents are not related to the spectrum type, nor do they depend on the

344   grain size (Tables 1 and 3). The portion of water ascribed to Ti-related substitutions

345   (Table 3) is highly variable and ranges from about 5 to 75 % of the total water content,

346   depending on the spectrum type. For spectrum types A, B, and C, 'Ti-related' water

347   makes up roughly 50 % of the total water content. Higher 'Ti-related' water contents (up

348   to 75 %) may be present in samples characterized by spectrum type D, and lower

349   contents of 5-20 % may be associated with spectrum type E.

350

351   **Correlation of water and Ti**

352

353   Several authors stated that Ti and water concentrations in natural olivine are not

354   correlated (e.g., Kurosawa et al. 1997; Gose et al. 2008). The same result is found in the

355   present study if Ti contents are compared only to the total water contents (Fig. 4a).

356   However, if the spectrum type is considered, compositional systematics become obvious

357   and the previous statement is no longer valid. Samples characterized by spectrum type

358   D accommodate the highest proportion of water in Ti-related defects. These samples, in

359   fact, reveal the highest relative Ti-contents (Fig. 4a, Table 3), with Ti (μmole/g) $\geq$ H/2

360   (μmole/g). In contrast, 'spectrum type E samples' – all coexisting with amphibole -

361   incorporate the least fraction of water in Ti-related defects. These samples, indeed, are

362   characterized by the lowest relative Ti contents, with Ti (μmole/g) << H/2 (μmole/g).

363   Samples with spectra types A, B, and C are consistent with this observation as the Ti-

364   related amount of water increases from A to C as well as the relative Ti content of the

365   samples (i.e., Ti versus H/2 in μmole/g; Fig. 4a).

366

367   The above comparison implies that a correlation between Ti and water is unlikely if the

368   sample set includes olivines with different types of IR absorption spectra. However, if

369   only the peaks at 3572 and 3525 cm^{-1} in the IR absorption patterns are caused by 'Ti-

370   related' defects, i.e., the substitution $Mg^{2+} + Si^{4+} = Ti^{4+} + 2\,H^{+}$, then Ti in olivine should

371   only correlate with the fraction of water involved in this substitution (see Table 3).

372

373   Hence, a plot of Ti versus H/2 in 'Ti defects' (Fig. 4b) should be used for comparing

374   water and Ti contents. If Ti incorporation in olivine is solely governed by the above

375   substitution, and if, vice versa, the peaks at 3572 and 3525 cm^{-1} are exclusively caused

376   by water in Ti-related defects, a 1 : 1 correlation line should result, provided no

377   secondary water loss occurred. Samples affected by water loss should then easily be

378   identified by Ti contents exceeding H/2. Figure 4b reveals six olivine samples plotting at

379   or close to the 1 : 1 correlation line and eight samples that plot moderately or significantly

380   above it. The former samples should have preserved their original water content, at least

381   that fraction incorporated via Ti-related substitutions. Presumably, the latter samples

382   experienced different degrees of water loss; for an estimate see Table 3. However, it

383   cannot be excluded that originally they contained less water than predicted by the Ti

384   contents because a substitution of Ti for Si is possible in olivine (Hermann et al. 2005;

385   Berry et al. 2007a).

386

387   If the substitution model is correct, samples should not have Ti contents lower than H/2.

388   Figure 4b shows that only one sample (with overall low H and Ti contents) plots

389   somewhat below the line. Hence, the results of our study can be reconciled with the

390   substitution model $Mg^{2+} + Si^{4+} = Ti^{4+} + 2\,H^{+}$.

391

392

393   **COMPARISON WITH LITERATURE DATA**

394

395   Water contents of olivine from spinel peridotite xenoliths were determined for a number

396   of occurrences worldwide (for references see 'Introduction' and Table 4). Literature data

397   comprising concentrations of water and other trace elements in natural olivine, however,

398   are still limited. The most relevant published data for olivine from basalt-hosted spinel

399   peridotite xenoliths, summarized in Table 4, are discussed below and compared with our

400   results. Data from kimberlite-hosted types and garnet peridotite xenoliths are included

401   only for comparison and are not discussed in detail.

402

403   Available data imply that low water content is typical for olivine from basalt-hosted spinel

404   peridotite xenoliths and oceanic spinel peridotites. Considering only results from IR

405   spectroscopic measurements, excluding data inferred from coexisting pyroxene (see

406   Table 4), the highest water content is 16 ppm (Kent and Rossman 2002; Falus et al.

407   2008). In most cases, the maximum contents are below 10 ppm (Miller et al. 1987;

408   Peslier and Luhr 2008; Yang et al. 2008; Gose et al. 2009; Soustelle et al. 2010;

409   Schmädicke et al. 2011). Comparably high water contents of 10-39 ppm were

410   determined by secondary ion mass spectrometry (Kurosawa et al. 1997) for samples

411   from various locations, including two Eifel samples. The water contents of the latter

412   samples are 10 ppm (Dreiser Weiher) and 18 ppm (Meerfelder Maar), respectively,

413   matching the analyses of the present study nicely. The same applies to the Li

414   concentrations (1.8 and 2.1 ppm) that overlap with the results of the present study (1.4-

415   3.1 ppm).

416

417   From the studies listed above it appears that olivine water contents are unrelated to the

418   tectonic setting of the host peridotite, i.e. within-plate sub-continental or plate-margin

419   supra-subduction zone mantle. However, the database is small and setting-related

420   characteristics might be obscured by differential water loss. No data exist for olivine from

421   sub-oceanic mantle peridotite, except that water content is below the detection limit of <1

422   ppm (Table 4). This is probably a result of secondary water loss due to slow tectonic

423   exhumation. However, orthopyroxene presumably preserved the original water contents

424   (Gose et al. 2011) and can be used for a preliminary estimate of the water content in

425   olivine. With an orthopyroxene-olivine partition coefficient of 6.7 (Kovács et al. 2012),

426   original water contents of 40 and 2 ppm are obtained for olivine of sub-oceanic peridotite

427   from two different sites at the Mid-Atlantic Ridge (Table 4).

428

429   The generally low water contents in olivine from spinel peridotites are probably not the

430   original mantle contents but were modified by decompression-related water loss during

431   ascent. This is evident from the positive correlation between water content and grain

432   size, and from concentrations depending on grain area (i.e., core or rim) as documented

433   by Peslier and Luhr (2006) and Soustelle et al. (2010). In addition, Yang et al. (2008)

434   ascribe the very low contents of 0-2 ppm in olivine to water loss caused by the fast

435   diffusion of H in olivine compared to that in both pyroxenes. Their conclusion is based on

436   data of coexisting ortho- (up to 155 ppm) and clinopyroxene (355 ppm) that were utilized

437   to calculate the primary equilibrium water contents for olivine (0-35 ppm). Moreover, the

438   non-equilibrium distribution of water between olivine and pyroxene, described above for

439   oceanic peridotite, may be explained by differential water loss in olivine and pyroxene.

440

441   Judging from the infrared spectra published in the literature, the two 'Ti peaks' seem to

442   be the typical feature shared by many, if not most, investigated olivines. In addition, the

443   two peaks are the most prominent ones in the majority of recorded spectra. However,

444   there are also samples in which these peaks are lacking such as in samples from

445 Romania (Falus et al. 2008) and Kenya (Miller et. al. 1987). In these cases, the main

446 bands occur in the range 3300-3450 cm^{-1}. Olivine in xenoliths from Kamchatka derived

447 from the supra-subduction zone mantle also has the main peaks in the 3300-3400 cm^{-1}

448 range, but with an additional weak peak at 3572 cm^{-1} (Soustelle et al. 2010).

449

450 Data for both water and trace elements concentrations, needed to recognize possible

451 correlations between water content or IR spectrum type and crystal chemistry, are given

452 only in a few studies. Contents of B and Li were determined on four olivine samples from

453 different continents but no correlation with the water content was found (Kent and

454 Rossman 2002). Kurosawa et al. (1997) also observed no correlation between water and

455 trivalent cations in olivine from spinel peridotite (18 samples) but garnet peridotite

456 samples (9) did reveal a positive correlation. These authors concluded that trivalent

457 cations are incorporated in spinel-peridotite-facies olivine by the Tschermak's

458 substitution and not by a substitution involving hydrogen. However, the increasing

459 evidence (see above) of water loss in olivine from spinel peridotite, compared to garnet

460 peridotite, may also explain the observations.

461

462 Comparative studies of water in olivine from amphibole-bearing and amphibole-free

463 peridotites are rare. Recently, Yang et al. (2008) came to the conclusion that water

464 contents of both olivine and pyroxene do not correlate with the presence or absence of

465 amphibole. In fact, the only water-free olivine was derived from an amphibole peridotite,

466 and the olivine richest in water (35 ppm) was found in an amphibole-free peridotite. The

467 results of the present study are very similar to the findings of Yang et al. (2008). The

468 water-poorest olivine from the Eifel (10 ppm) was found in an amphibole-bearing

469 peridotite, whereas the water-richest olivine (21 ppm) was derived from a 'dry' peridotite.

470

471   The literature data on water contents in olivine fit in well with the results of the present

472   study. In general, olivine from spinel peridotites contains comparably low water

473   concentrations, regardless of geological setting. The maximum values, however, are

474   variable reaching only c. 6-8 ppm in some areas and c. 35 ppm in others. Our maximum

475   contents of 21 ppm are close to the data from samples from Romania (Falus et al. 2008).

476   However, our spectra types are different compared to the Romanian olivines but

477   compare well with the spectra presented by Peslier and Luhr (2006). A relation between

478   spectrum type and geological setting is presently not visible.

479

480   Considerably more water is present in olivine from kimberlite-hosted mantle xenoliths,

481   most of which are garnet peridotites (e.g., Miller et al. 1987; Bell and Rossman 1992).

482   For instance, olivine from South African xenoliths contains 60-150 ppm water (Kent and

483   Rossman 2002). Higher contents of up to 300-400 ppm were determined for olivine

484   megacrysts from South African kimberlites (Bell et al. 2004), xenolithic olivine (Matsyuk

485   and Langer 2004) and olivine xenocrysts (Koch-Müller et al. 2006), both from Siberian

486   kimberlites. Although lower water contents may be typical of olivine from cratonic garnet

487   peridotite (i.e., 0-80 ppm; Peslier et al. 2010), the maximum water contents in olivine

488   from garnet peridotite xenoliths (c. 400 ppm) are one order of magnitude higher

489   compared to spinel peridotite xenoliths (35 ppm). Moreover, olivine from spinel peridotite

490   is also characterized by lower Ti concentrations (20-80 ppm) compared to olivine from

491   garnet peridotite (50-280 ppm; Berry et al. 2005). In contrast, other trace elements such

492   as Li and B (Kent and Rossman 2006; Koch-Müller et al. 2006; this study) have

493   comparable contents in both rock types. The great difference in water contents between

494   spinel and garnet peridotite may be due to two reasons: (i) the pressure-enhanced water

495   storage capacity, and (ii) water loss due to different uplift velocities. The majority of

496   garnet peridotite xenoliths are transported by kimberlite whereas most spinel peridotites

497   are basalt-hosted. Kimberlite-hosted mantle xenoliths, because of faster upward

498   transport, preserve the original water much better than basalt-hosted ones (Peslier and

499   Luhr 2006; Peslier et al. 2008). Differential uplift velocities will enhance the original,

500   pressure-related differences in water contents between garnet and spinel peridotites.

501   The recent findings imply that pyroxenes are better suited than olivine to infer the

502   mantle's water budget.

503

504

505   **DISCUSSION AND CONCLUSIONS**

506

507   **General findings**

508

509   The investigated olivine samples from basalt-hosted spinel peridotite xenoliths contain

510   water in the range of <1-21 ppm. Such low concentrations were reported from several

511   other studies on equivalent samples and interpreted as a result of water loss (e.g.,

512   Peslier and Luhr 2006). In the present study, we consider water contents between 16

513   and 21 ppm as original mantle values typical for olivine from depleted spinel peridotite

514   from the uppermost mantle, whereas water contents of ≤15 ppm were probably caused

515   by water loss (see below).

516

517   Each sample displays at least six different bands in the IR absorption spectra. The two

518   bands at 3572 and 3525 cm^{-1} that are ascribed to Ti-related point defects and the bands

519   at 3485, 3542 and 3597 cm^{-1} being associated with Si vacancies are displayed by all

520   samples. Differences in the absorption patterns occur in the low frequency range (i.e.,

521   3100-3450 cm^{-1}) and are the basis to distinguish 5 spectra types, A, B, C, D, and E.

522   Bands ascribed to Mg site vacancies (i.e., 3100-3300 cm^{-1}) and those associated with

523   trivalent cations (i.e., 3300-3400 cm^{-1}) are present in most spectra, except of D.

524   Comparing the spectra, the peaks in the 3300-3400 cm^{-1} interval seem to correlate in

525   intensity with those in the 3100-3300 cm^{-1} range (moderate size in spectra A, B, E; small

526   in C, and absent in D). Berry et al. (2005) noted that water in Ti-related defects is

527   primary, while Fe^{3+} related bands are diagnostic of oxidation and secondary processes. If

528   true, the observed correlation of ‚Mg vacancy peaks' and those involving trivalent cations

529   suggests that both are non-primary features but due to secondary processes.

530

531   Our study confirms the suggestion (e.g., Berry et al. 2005; Walker et al. 2007) that H

532   incorporation associated with Ti is the most important mode of water storage in olivine

533   from the shallow upper mantle. A possible exception is olivine that equilibrated with

534   amphibole. Spectrum E is restricted to amphibole-bearing xenoliths (three Eifel samples).

535   This spectrum indicates only a small fraction of water possibly related to Ti point defects

536   and a similar small quantity that may be bound to planar Ti defects. The dominant

537   absorption bands occur in the low frequency range suggesting other substitution

538   mechanisms (e.g., coupled substitutions with trivalent cations).

539

540   The present results also indicate that water and Ti contents of natural olivine from spinel

541   peridotites are related. A correlation, however, may only become obvious if the fraction of

542   water associated with 'Ti defects' is considered instead of the total water content of

543   olivine, as shown in Fig. 4b. The analytical data of this study confirm the model

544   substitution $Ti^{4+} + 2H^+ = Mg^{2+} + Si^{4+}$ proposed in the literature (Berry et al. 2006, 2007a;

545   Walker et al. 2007). We suggest that the Ti content of olivine may be used to estimate

546   the maximum amount of water that can be incorporated by this substitution. The latter,

547   calculated value, compared to the measured content of water that is bound to Ti-related

548   defects, may be useful to infer the degree of water loss (Fig. 4b; Table 3). Applied to the

549   investigated olivines, five samples show no or only little water loss. The total water

550   contents in these olivines are in the range of 16-21 ppm. The remaining twelve samples

551   may have lost variable amounts of their original water in the range from 36 to >80 %.

552   These olivines have lower water contents ranging from <1 to 15 ppm. This approximation

553   provides an upper limit for water loss because it supposes that Ti in olivine is exclusively

554   incorporated by the above substitution.

555

556   The intensity of the peaks in the range of 3300-3400 cm^{-1} or, more precisely, the fraction

557   of water calculated for this range (not shown) does not correlate with the contents of

558   trivalent cations in olivine. This does not contradict the assumption that part of the water

559   in olivine is incorporated via a coupled substitution involving trivalent cations. It merely

560   indicates that other substitutions are probably more important for the incorporation of

561   trivalent cations in olivine than the coupled substitution with H. This is also in accordance

562   with the several hundreds ppm concentration of trivalent cations as compared to only a

563   few ppm H associated with the 3300-3400 cm^{-1} range in the IR spectrum.

564

565   The content of the most abundant trivalent cations, Al + Cr, correlates with Ca (Fig. 2a)

566   implying that their concentration in olivine is primarily controlled by P and T and not by

567   water fugacity. The Ca content in olivine has been used as a geothermobarometer (Brey

568   and Köhler 1990) and is very important to infer equilibrium conditions for garnet-free

569   spinel peridotites (e.g., Will et al. 2010). The positive correlation of Ca with Al + Cr

570   implies that the Al + Cr totals of olivine are potentially useful for thermobarometry.

571

572   **Amphibole and olivine water content**

573

574   The presence of amphibole, observed in three of the Eifel samples and in the sample

575   from Austria, does not lead to high water contents in coexisting olivine. On the contrary,

576   the water-poorest Eifel olivine was derived from an amphibole-bearing peridotite,

577   whereas the water-richest olivine was found in an amphibole-free peridotite. Other trace

578   elements may help to explain this observation. Obviously, the presence of amphibole in

579   the investigated spinel peridotite xenoliths is related to rather low Ca, Al, Cr, and V

580   contents in coexisting olivine. The Ti contents of olivine in two of the amphibole-bearing

581   samples are also very low (3.8 and 4.5 ppm), but intermediate in the other two samples

582   (13 and 26 ppm).

583

584   Formation of amphibole in peridotite is commonly related to infiltration of water-rich fluid

585   and/or interaction with alkali basaltic or carbonatitic melts (e.g., Coltorti et al. 2007; Witt-

586   Eickschen et al. 2003). Fluid not only triggers amphibole formation but it also should

587   equilibrate with the nominally anhydrous minerals in peridotite, namely olivine and

588   pyroxene. Interestingly, olivine in the amphibole-bearing samples does not seem to have

589   incorporated water as a result of fluid infiltration, presumably due to unfavorable pressure

590   and/or temperature. Of course, minerals either take up water if they are under-saturated,

591   or lose water if they previously equilibrated at higher pressures and/or temperatures

592   under water-saturated conditions. The relatively low contents of Ca and Al + Cr in the

593   amphibole-bearing samples, compared with the 'dry' samples, suggest fluid infiltration

594   and re-equilibration at comparably low pressure and/or temperature. This conclusion

595   agrees with previously estimated temperatures of 800-1000°C for amphibole-bearing and

596   1000-1300°C for 'dry' peridotites from the Eifel (Witt-Eickschen 2007). We suggest that

597   re-equilibration of the whole assemblage occurred during amphibole formation and

598   presumably led to water loss including loss of further trace elements such as Ca, Al, Cr,

599   V, and Ti in olivine. Simultaneously, re-distribution of water in the olivine structure

600 occurred as documented by the observed change in relative peak intensities. Spectrum

601 type E, restricted to amphibole-bearing samples, suggests that very little (if any) water is

602 bound to Ti related defects. This is in contrast to most other investigated olivines,

603 displaying spectra A to D, that accommodate a large fraction of, or even all, water in Ti

604 related defects.

605

606

607   **ACKNOWLEDGMENTS**

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863   **Figure captions**

864

865   **FIGURE 1.** Polarized IR absorption spectra measured parallel to the crystallographic a-

866   and c-axis, baseline-corrected and deconvoluted into single Gaussian- and Lorentzian-

867   shaped bands.

868

869   **FIGURE 2.** Variation diagrams showing selected trace element concentrations in olivine.

870   The data correspond to the sample averages given in Table 2b; the regression lines

871   were calculated with Excel. a. Plot of Ca versus Al + Cr; b. Plot of Ca versus Al; c. Plot of

872   Sc versus Ca; d. Plot of V versus Ti. See text for further information.

873

874   **FIGURE 3.** Five different types of IR absorption spectra (A, B, C, D, and E) measured

875   with IR radiation polarized parallel to the crystallographic a-axis (bold black lines), b-axis

876   (bold gray lines) and c-axis (thin black lines). The spectra are normalized to 1 cm sample

877   thickness.

878

879   **FIGURE 4.** Plot of Ti versus H/2. Values are given in μmole/g in order to evaluate the

880   coupled substitution $Mg^{2+} + Si^{4+} = Ti^{4+} + 2\ H^+$ as potential mechanism for H incorporation

881   in the investigated olivines. a. Plot of Ti versus total hydrogen (H/2) in olivine. b. Plot of Ti

882   versus hydrogen (H/2) calculated from the 'Ti peaks' (i.e., 3572 and 3525 cm^{-1}) as given

883   in Table 3. See text for further explanation.

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TABLE 1. Investigated olivine samples from spinel peridotite xenoliths.

Locality	Sample number	Amphibole present ?	Olivine grain size [mm]
Eifel, Dreiser Weiher	E-2	no	2-3
Eifel, Dreiser Weiher	E-5	no	2-3
Eifel, Dreiser Weiher	E-194	yes	1-2
Eifel, Dreiser Weiher	E-196	no	2
Eifel, Dreiser Weiher	E-211	yes	1
Eifel, Dreiser Weiher	E-213	yes	1-1.5
Eifel, Dreiser Weiher	E-D58	no	1-2
Eifel, Dreiser Weiher	E-K1	no	2
Eifel, Leyendecker Grube	E-LG	no	1.5-2
Fichtelgebirge, Hirschentanz	F-HT	no	2-2.5
Fichtelgebirge, Teichelberg	F-TB	no	2-2.5
Fichtelgebirge, Zinster Kuppe	F-ZK	no	2-2.5
Austria, Kapfenstein	Kapf	yes	2.5-3
Mongolia	Mo-21	no	1-2
Mongolia	Mo-22	no	2-3
Mongolia	Mo-8531	no	2
Nigeria	Nig	unknown	10

TABLE 2a. Selected microprobe analyses of olivine samples in wt.-%. Cations were calculated on the basis of 4 oxygen atoms and by treating all Fe as Fe^{2+}.

	E-2-3	E-5-2	E-194	E-196-4	E-211-1	E-213	E-D58-2	E-K1-6	E-LG-2
	ol5	ol4	ol5	ol1	ol7	ol5	ol4	ol1	ol8
SiO_2	40.67	41.06	40.61	39.88	39.84	40.88	40.34	40.99	40.27
TiO_2	0.01	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.01
Cr_2O_3	0.05	0.03	0.00	0.04	0.01	0.05	0.03	0.00	0.02
NiO	0.36	0.33	0.35	0.33	0.35	0.40	0.30	0.34	0.32
FeO	8.11	8.50	8.56	10.08	9.06	8.36	8.66	8.26	8.59
MnO	0.11	0.12	0.10	0.15	0.14	0.15	0.13	0.12	0.12
MgO	50.54	50.54	49.94	48.91	50.66	50.16	51.23	50.24	50.37
CaO	0.13	0.13	0.07	0.13	0.05	0.06	0.12	0.13	0.13
Total	99.97	100.71	99.63	99.52	100.11	100.06	100.81	100.09	99.83
Si	0.992	0.995	0.995	0.987	0.976	0.996	0.979	0.998	0.986
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.001	0.000	0.000	0.001	0.000	0.001	0.000	0.000	0.000
Ni	0.007	0.006	0.007	0.007	0.007	0.008	0.006	0.007	0.006
Fe	0.165	0.172	0.175	0.209	0.186	0.171	0.176	0.168	0.176
Mn	0.002	0.002	0.002	0.003	0.003	0.003	0.003	0.002	0.002
Mg	1.837	1.825	1.824	1.804	1.850	1.823	1.853	1.823	1.839
Ca	0.003	0.003	0.002	0.004	0.001	0.002	0.003	0.003	0.003
Total	3.008	3.005	3.005	3.013	3.024	3.003	3.021	3.002	3.014

Mg#	0.917	0.914	0.912	0.896	0.909	0.914	0.913	0.916	0.913

	F-HT-1	F-TB-1	F-ZK-2	Kapf-2	Mo-21-3	Mo-22-3	Mo-8531	Nig
	ol4	ol3	ol1	ol	ol	ol	ol	ol
SiO_2	40.75	40.27	40.43	41.01	40.77	41.10	40.69	40.92
TiO_2	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01
Cr_2O_3	0.02	0.03	0.01	0.02	0.02	0.02	0.00	0.00
NiO	0.40	0.33	0.39	0.41	0.40	0.37	0.36	0.35
FeO	8.64	8.86	8.64	8.92	10.49	9.86	9.24	8.67
MnO	0.15	0.16	0.13	0.13	0.15	0.18	0.14	0.14
MgO	50.01	49.66	49.76	49.70	48.56	49.23	49.01	49.96
CaO	0.07	0.09	0.05	0.07	0.06	0.09	0.04	0.09
Total	100.02	99.38	99.42	100.26	100.45	100.84	99.47	100.14
Si	0.995	0.991	0.994	1.000	0.999	1.000	1.001	0.998
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ni	0.008	0.006	0.008	0.008	0.008	0.007	0.007	0.007
Fe	0.176	0.182	0.178	0.182	0.215	0.201	0.190	0.177
Mn	0.003	0.003	0.003	0.003	0.003	0.004	0.003	0.003
Mg	1.820	1.822	1.823	1.806	1.774	1.785	1.797	1.816
Ca	0.002	0.002	0.001	0.002	0.002	0.002	0.001	0.002
Total	3.005	3.008	3.006	3.000	3.001	3.000	2.999	3.002
Mg#	0.912	0.909	0.911	0.908	0.892	0.899	0.904	0.911

TABLE 2b. Trace element concentrations of olivine in ppm determined by Q-LA-ICP-MS. The data are sample averages based on 4 analyses. Be and rare earth elements have concentrations below the detection limit.

	E-2	E-5	E-194	E-196	E-211	E-213	E-D58	E-K1	E-LG
Li	1.7	1.7	3.1	2.1	2.6	2.7	1.7	1.5	1.4
B	2.1	1.7	1.8	1.2	1.9	1.9	1.9	1.7	2.3
Al	253	356	109	362	56	64	329	344	275
P	98	92	97	94	97	96	94	98	84
Ca	909	998	510	900	363	409	872	890	837
Sc	4.0	4.4	2.7	3.8	2.3	3.2	3.9	3.9	3.9
Ti	28	23	26	51	3.8	4.5	31	41	18
V	7.2	5.8	2.8	6.2	2.0	2.5	5.3	5.4	6.8
Cr	362	243	139	152	85	126	223	226	263
Mn	816	992	1009	1082	1048	977	941	920	995
Co	158	156	146	162	145	155	152	154	151
Ni	3376	3288	3267	3034	3115	3396	3163	3244	3115
Ga	0.11	0.14	0.07	0.15	0.07	0.07	0.10	0.14	0.08
Ge	0.90	0.81	0.89	0.80	0.60	0.68	0.78	0.91	<0.6
Y	0.05	0.06	0.04	0.08	0.02	0.04	0.07	0.08	0.02

	F-HT-1	F-TB-1	F-ZK-2	Kapf-2	Mo-21	Mo-22	Mo-8531	Nig
Li	1.7	1.5	1.5	1.8	2.0	2.3	2.1	1.6
B	1.8	1.3	1.9	1.7	0.9	1.4	1.2	1.3

Al	126	159	108	87	70	265	66	188
P	95	87	89	98	88	100	87	66
Ca	486	580	452	409	314	662	299	675
Sc	3.2	3.6	3.2	2.6	2.1	3.4	2.2	3.5
Ti	12	3.7	7.7	13	23	39	26	66
V	3.6	3.4	3.7	2.3	2.0	4.5	2.1	6.0
Cr	183	147	126	74	28	117	31	185
Mn	989	952	965	980	1028	1040	1002	956
Co	154	151	146	157	167	167	149	148
Ni	3318	3298	3161	3279	3399	3311	3176	3141
Ga	0.07	<0.06	0.06	<0.06	0.08	0.17	0.06	0.09
Ge	0.90	0.80	0.66	0.77	0.69	0.83	0.75	0.97
Y	0.02	0.02	0.02	0.02	0.03	0.04	0.03	0.07

TABLE 3. Spectrum type, total water content in olivine and water content calculated from the intensity of the 'Ti peaks' at 3572 and 3525 cm^{-1}. Water in 'Ti peaks' is also given as H in μmole/g for better comparison with the Ti content of olivine (also given in μmole/g). See text for further explanation.

Sample number	Spectrum type	H_2O total [wt.-ppm]	H_2O in 'Ti peaks' [ppm]	H in 'Ti peaks' [μmole/g]	Ti [μmole/g]	Possible H_2O loss [%]
E-2	A	21	9.4	1.04	0.59	12
E-5	B	11	5.5	0.61	0.48	36
E-194	E	15	2.1	0.23	0.54	78
E-196	C	13	6.6	0.73	1.06	65
E-211	E	17	3.3	0.37	0.08	0
E-213	E	10	0.5	0.06	0.09	71
E-D58	C	18	12.0	1.33	0.65	0
E-K1	C	10	5.6	0.62	0.86	64
E-LG	B	18	7.1	0.79	0.37	0
F-HT	-	<1	<1	<0.1	0.26	>80
F-TB	-	<1	<1	<0.1	0.08	>35
F-ZK	-	<1	<1	<0.1	0.16	>69
Kapf	A	16	5.1	0.57	0.27	0
Mo-21	D	9	3.9	0.43	0.48	53
Mo-22	D	11	5.9	0.66	0.82	60
Mo-8531	D	4	3.0	0.33	0.54	69
Nig	D	14	9.0	1.00	1.40	64

TABLE 4. Water contents in olivine from upper mantle spinel peridotites. The samples from intra-continental and continental arc settings are all basalt-hosted xenoliths. The oceanic spinel peridotites are drill-hole samples. With the exception of Kurosawa et al. (1997), all data were collected by IR spectroscopy.

Locality	Comment, sample number	H_2O content [ppm]	Main peaks [cm^{-1}]	Reference
various	intra-continental xenoliths, 12	<1-6	3572, 3525 (most samples), 3300-3400 (Kenya sample)	Miller et al. (1987)
Tanzania, Kenya, Australia, China	intra-continental xenoliths and xenocrysts, 4	0.8-16 (3 samples) 34 (Kenya sample)	not given	Kent and Rossman (2002)
Mexico, Washington State	intra-continental xenoliths, 17	0-6.8	3571, 3562, 3541, 3525, 3480 (all samples)	Peslier and Luhr (2006)
Romania	intra-continental xenoliths, 7	2.1-15.4	3300-3450	Falus et al. (2008)
North China Craton	intra-continental xenoliths, some with amphibole, 27	0-2 * 0-35 [§]	3600 (unpolarized measurements)	Yang et al. (2008)
Kamchatka	continental arc	1-8.6	3300-3400, weak	Soustelle et al.

	xenoliths, 26		peak at 3572	(2010)
Japan, Australia, San Carlos, Eifel	intra-continental and continental arc xenoliths, 18	10-39	data obtained by secondary ion mass spectrometry	Kurosawa et al. (1997)
Mid-Atlantic Ridge, 23° N	oceanic peridotite	<1 * 40 #	no peaks detected	Gose et al. (2009)
Mid-Atlantic Ridge, 15° N	oceanic peridotite	<1 * 2 #	no peaks detected	Schmädicke et al. (2011)

Notes: * Measured values; § Calculated from water in clinopyroxene by applying a partition coefficient of 10. # Calculated from water in orthopyroxene applying an orthopyroxene- olivine partition coefficient of 6.7 (Kovács et al. 2012).