Water contents of nominally anhydrous orthopyroxenes from oceanic peridotites determined by SIMS and FTIR

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Abstract
This study presents new secondary ion mass spectrometry (SIMS) reference materials (RMs) for measuring water contents in nominally anhydrous orthopyroxenes from upper mantle peridotites. The enstatitic reference orthopyroxenes from spinel peridotite xenoliths have Mg#s between 0.83 and 0.86, Al2O3 ranges between 4.02 and 5.56 wt%, and Cr2O3 ranges between 0.21 and 0.69 wt%. Based on Fourier-transform infrared spectroscopy (FTIR) characterizations, the water contents of the eleven reference orthopyroxenes vary from dry to 249 ± 6 µg/g H2O. Using these reference grains, a set of orthopyroxene samples obtained from variably altered abyssal spinel peridotites from the Atlantic and Arctic Ridges as well as from the Izu-Bonin-Mariana forearc region was analyzed by SIMS and FTIR regarding their incorporation of water. The major element composition of the sample orthopyroxenes is typical of spinel peridotites from the upper mantle, characterized by Mg#s between 0.90 and 0.92, Al2O3 between 1.66 and 5.34 wt%, and Cr2O3 between 0.62 and 0.96 wt%. Water contents as measured by SIMS range from 68 ± 7 to 261 ± 11 µg/g H2O and correlate well with Al2O3 contents (r = 0.80) and Cr#s (r = -0.89). We also describe in detail an optimized strategy, employing both SIMS and FTIR, for quantifying structural water in highly altered samples such as abyssal peridotite. This approach first analyzes individual oriented grains by polarized FTIR, which provides an overview of alteration. Subsequently, the same grain along with others of the same sample is measured using SIMS, thereby gaining information about homogeneity at the hand sample scale, which is key for understanding the geological history of these rocks.

Keywords FTIR · Hydrogen · Nominally anhydrous minerals · Orthopyroxene · SIMS · Spinel peridotite

Introduction
Understanding the role of water, its amount and distribution in the Earth’s upper mantle and its influence on convective processes and geodynamics is a key task of igneous geochemistry. Water decreases the mantle’s viscosity and mechanical strength via hydrolytic weakening of olivine (Demouchy et al. 2012; Tielke et al. 2017) and lowers peridotite melting temperatures (e.g. Hirth and Kohlstedt 1996), thereby affecting melting depth and thus the composition of the melt (Hauri et al. 2006).

Incorporated by various substitutions, such as protons attached to oxygen anions forming “hydroxyl defects” in the crystal structure (Bell and Rossman 1992; Libowitzky and Beran 2006), small amounts of water can be found in nominally anhydrous minerals (NAMs) such as pyroxenes and olivines derived from the Earth’s upper mantle. Olivine is believed to dehydrate rapidly (e.g. Mackwell and Kohlstedt 1990) when decompressed during tectonic uplift or magmatic transport to the surface as recorded by core-rim zonation in natural grains (Demouchy et al. 2006; Peslier and Luhr 2006; Schmädicke et al. 2013). Although H loss has recently been observed in pyroxenes as well (Tian et al. 2016; Denis et al. 2018), orthopyroxene is generally considered to retain its upper mantle water concentration during exhumation (Gose et al. 2011; Hao et al. 2014; Azevedo-Vannson et al. 2021) and can be used as a reliable tracer for water in the upper mantle (Denis et al. 2013; Warren and

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A number of studies on experimental and natural orthopyroxene have shown that the mineral can hold up to several hundred µg/g H$_2$O, making it a significant reservoir for water in the upper mantle (Bell and Rossman 1992; Hirschmann et al. 2005; Peslier 2010).

Several laboratory methods are capable of quantifying hydrogen in NAMs: vacuum manometry is an easily available technique but is also destructive and requires large enough alteration-free sample volumes (Aubaud et al. 2007), which can be problematic in the case of NAMs in upper mantle rocks. Nuclear reaction analysis (NRA) and elastic recoil detection analysis (ERDA) are also reliable techniques for determining hydrogen contents in mantle minerals (Bell et al. 2003; Withers et al. 2012) but the necessary facilities are often difficult to access (Aubaud et al. 2007). More widespread spectroscopic approaches such as nuclear magnetic resonance (NMR; Rauch and Keppler 2000; Kohn 2006) are difficult to use when iron is present in the matrix (Aubaud et al. 2007). A more detailed review of the different methods is given by Rossman (2006) and recent analytical advances are also discussed in Sheng et al. (2016).

For these reasons, FTIR has long been the method of choice for investigating the hydrogen distribution in NAMs (Rossman 2006; Mosenfelder et al. 2011). In contrast to other techniques, the method itself (after sample preparation) is non-destructive and yields information about the vibrational energy and orientation of OH-dipoles in the crystal structure. It can thus distinguish structurally incorporated hydrogen from water contained in impurities such as secondary hydrous phases, alteration products or fluid inclusions (Rossman 1996; Libowitzky and Beran 2004). Numerous studies have taken advantage of this specificity to document trace amounts of structurally bound water in olivine, ortho-, and clinopyroxene from abyssal peridotites which are often overprinted by alteration (Gose et al. 2009, 2011; Peslier 2010; Schmädicke et al. 2011, 2018; Hesse et al. 2015; Gose and Schmädicke 2021). Generally, there are different approaches when using infrared spectroscopy: (i) analysis of oriented crystals using polarized radiation or (ii) analysis of unoriented crystals using unpolarized radiation (statistical method). Regarding the first method, the orthopyroxene grains in abyssal peridotites are either very small or broken into fragments, which makes it difficult to prepare oriented crystals to be analyzed by polarized radiation. For analyzing randomly oriented crystals using unpolarized radiation one would need to examine a large number of grains in order to get a statistically robust representation of the sample. In contrast to xenoliths, abyssal peridotites are often highly altered, i.e. serpentinized and exhibit a typical porphyroclastic texture, meaning there are often only two or three individual orthopyroxene grains available when preparing sections of hand samples. Even if one were able to find enough individual grains, with this method one would get the average water content for the sample with little or no information about the heterogeneity of the material. In either case, sample preparation for FTIR can be difficult and time-consuming and strongly depends on sample quality and size. Moreover, there are significant, unresolved calibration issues regarding which molar absorption coefficients are appropriate (e.g. Mosenfelder and Rossman 2013) and there is no agreed procedure as to how the data should be processed (manual versus mathematical correction of absorption baseline), which can introduce major biases between data sets obtained by different working groups.

Because of these challenges, a number of recent studies have chosen SIMS as a means to quantify H$_2$O contents in NAMs (e.g. Warren and Hauri 2014; Kumamoto et al. 2017). This method offers the advantage of high spatial resolution, often better than 10 µm, and insensitivity to crystal orientation (Koga et al. 2003). The main drawback of SIMS is that it detects the bulk hydrogen content of a material, meaning it cannot distinguish between different water species. This, however, is important in the case of abyssal peridotites which commonly contain secondary hydrous phases. Moreover, SIMS cannot directly determine elemental concentrations - it can only compare the secondary ion signal from well-characterized reference to that from an “unknown” sample. Crucially, such SIMS RMs must be closely matrix-matched to the actual samples being tested. Thus, for SIMS one needs to first establish a calibration curve, preferably based on multiple, well-characterized RMs. Only once this has been achieved can meaningful analyses of actual samples be undertaken.

The aims of this study are to (i) identify reference orthopyroxene crystals that are well suited for calibrating SIMS, (ii) quantify H$_2$O concentrations in natural orthopyroxene samples using this calibration, (iii) compare our SIMS results to the results obtained independently by FTIR, and (iv) evaluate the methods in order to establish a robust methodology for determining intra-crystalline water contents in orthopyroxene recovered from abyssal peridotites (harzburgites), even when such material may have experienced extensive serpentinization.

### Materials and preparation

#### Orthopyroxene reference materials

Eight orthopyroxenes from spinel peridotites occurring as xenoliths in alkali basalts from Western Mongolia (hand samples Mo21, Mo22, and Mo8531) and three orthopyroxenes from spinel peridotites from the Eifel volcanic field in Western Germany (hand samples E-K1 and 1b-5) were selected for characterization as reference minerals. These peridotites consist of the four-phase assemblage olivine,
orthopyroxene, clinopyroxene, and spinel. For further details see Schmädicke et al. (2013) on samples from Western Mongolia and E-K1 and Stosch and Seck (1980) for sample 1b-5. The eleven, up to 3 mm sized orthopyroxene grains that were selected for use as RMs were optically clear and free of fractures.

### Orthopyroxene samples from abyssal peridotites

The twelve samples to be analyzed by SIMS include orthopyroxenes recovered from abyssal spinel peridotites (harzburgites) from various locations along the Mid-Atlantic Ridge (MAR), the Gakkel Ridge, Arctic Ocean, and the Izu-Bonin-Mariana forearc region (IBM; Table 1). The samples were recovered by either drilling (DSDP and ODP samples) or dredging and diving expeditions. Where large enough hand samples were available, thin sections were made on which the degree of serpentinization was assessed qualitatively (Fig. 1).

The rocks are moderately to highly altered. The primary mineral assemblage consists of olivine (ol), orthopyroxene (opx), brown spinel (spl), and minor clinopyroxene (cpx). In some samples olivine has been entirely replaced by serpentine, whereas in other samples fresh olivine kernels are preserved in the centers of concentric layers of serpentine (“mesh texture”). Orthopyroxene invariably forms up to mm-sized crystals, heavily broken into fragments, which are partially preserved (porphyroclastic texture). Most of the preserved orthopyroxene fragments contain amphibole lamellae, others are entirely altered or replaced by bastite. Primary clinopyroxene is rare to absent in these samples. Spinel grains formed interstitially, leading to highly irregular shapes. For further information on the petrology of the samples, see Regelous et al. (2016).

### Sample preparation

For the FTIR analyses, the peridotite reference orthopyroxenes were cut out of the hand samples using a saw. Xenoliths were slightly crushed and easily disaggregated thanks to their less compact structure. The RM grains were then prepared as cuboid bodies and polished on all six planar sides. The thickness of the cuboids was measured with a precision of ≤3 µm using an electronic micrometer and varied between 516 and 1746 µm.

Since the abyssal peridotite samples are highly altered and the orthopyroxene grains are commonly fragmented, few crystals suitable for FTIR analysis could optically be identified in the hand rock samples and thin sections. We therefore proceeded to crush (instead of sawing) selected rock portions. Because of their greater mechanical strength, the peridotite samples required crushing with severe force. Suitable orthopyroxene grain fragments, optically clear and without visible fractures, inclusions, and alteration products were hand-picked under a binocular microscope, individually embedded in epoxy, grinded down and polished on two sides. For the final polishing step a 3 µm diamond paste was used. This way, numerous orthopyroxene fragments from all samples could be prepared for FTIR analysis. The measurements were performed in three sessions in three randomly oriented but orthogonal planes. Sample thicknesses varied between 80 and 812 µm.

Upon having determined all water contents via FTIR, the RM Mo22-opx3 was dehydrated in a furnace at 1000 °C in air for 24 hours such that the grain could be used as a blank to determine the level of hydrogen background during the subsequent SIMS analyses. Dehydration was verified by FTIR according to the analytical procedure described below.

After completion of the FTIR analyses, pieces of the eleven reference grains were embedded in Epo-Tek®

| Sample | Lithology | Location | Degree of alteration |
|--------|-----------|----------|----------------------|
| ODP304-1309B-11R-1W | Serpentine with opx and ol relics | 30°N, Mid-Atlantic Ridge (Atlantis Massif) | very high |
| ODP304-1309B-11R-2W | Serpentinized harzburgite | 23°N, Mid-Atlantic Ridge | moderate |
| DSDP45-395-18R-1W-112 | Serpentinized harzburgite | 23°N, Mid-Atlantic Ridge | high |
| PS59-249-Br4 | n.a. | Gakkel Ridge | n.a. |
| ODP109-670A-4R-1W | Serpentinized harzburgite | 23°N, Mid-Atlantic Ridge | high |
| HLY-102-D32 | n.a. | Gakkel Ridge | n.a. |
| ODP125-0779A-26R-2W | Serpentinized harzburgite | Izu-Bonin-Mariana forearc region (Conical Seamount) | n.a. |
| PS55-75-30 | Serpentinized harzburgite | Arctic Ocean (Fram Strait) | high |
| ODP209-1272A-26R-1W-60-65 | Serpentinized harzburgite | 15°N, Mid-Atlantic Ridge | n.a. |
| PS59-236-80-500-900 | n.a. | Gakkel Ridge | n.a. |
| ME41/2-KD5-1 | Serpentine with opx relics | Southern Atlantic Ocean | very high |

n.a. indicates that no thin section was available for the respective sample.
Fig. 1 Plane-polarized (left) and cross-polarized (right) transmitted-light photomicrographs of thin sections from selected variably altered abyssal peridotite samples: a) ODP304 (IBM), b) DSDP45 (MAR), c) ODP109 (MAR), d) PS55-75 (Arctic Ocean), e) ME41/2 (Southern Atlantic Ocean)
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EPMA analysis

All major-element analyses were performed using a JEOL JXA-8200 electron microprobe equipped with five wavelength dispersive spectrometers. The analyses were run at a 15 kV acceleration voltage and a 15 nA probe current. A ~5 µm beam diameter was used for Na, whereas a <1 µm diameter was used for all other elements. Peak and background counting times were 20 s each. The following elements were analyzed: Al₂O₃ (Al), Cr₂O₃ (Cr), Fe₂O₃ (Fe), MgO (Mg), MnSiO₃ (Mn), albite (Na), NiO (Ni), rutile (Ti), and sphalerite (Zn). Kα lines were analyzed for all elements. 

SIMS calibration

Determinations of H₂O contents by SIMS were conducted using a Cameca 1280-HR instrument. The first series of analyses of the reference orthopyroxene crystals used a mass filtered ¹³³Cs⁺ primary ion beam with a total impact energy of 20 keV. ¹⁶O¹H⁻ ions were measured as a proxy for the hydrogen content as this molecule provided more stable within-run data than did ¹H²⁻. Despite the SIMS' high-vacuum conditions of 5 × 10⁻⁷ Pa in the sample chamber, we were unable to produce consistent ¹⁶O¹H⁻/¹⁸O⁻ ratios. Even the most hydrogen enriched RM (1b-5-opx1, 249 ± 6 µg/g H₂O according to FTIR) was affected by hydrogen...
adsorption onto the sample surface at the point of analysis during data acquisition. Much of this background could be attributed to electron-induced desorption of OH that resulted from the need to use low energy electron flooding when operating in negative secondary ion polarity.

Therefore, an alternative analytical set-up was tested using a duoplasmatron to generate $^{16}$O$^-$ as primary ions and recording the $^{28}$Si$^+$/$^{30}$Si$^+$ ion ratio. This alternative approach provided no advantages and was further complicated by an unstable primary ion current that dropped from roughly 2.0 nA to 0.8 nA during the analytical session. This resulted in an increase in the observed $^{28}$Si$^+$/$^{30}$Si$^+$ measured ratio as one would expect when hydrogen was mostly coming from vacuum contamination adsorbed during the analysis. We therefore decided it was necessary to remove all crystals from the epoxy and recast them in indium.

For the next series of analyses, the $^{16}$O$^-$ primary current was increased to 30 nA, the field of view was reduced to only 10 µm by closing the field aperture, and the primary beam raster was turned off. Furthermore, the positioning of external permanent magnets was adjusted such that H could be run as an ion rather than a molecule. A long duration liquid nitrogen cold trap was used during the run to improve the vacuum ($1.2 \times 10^{-7}$ Pa). Limit of detection under these conditions was around 5 to 10 µg/g $H_2O$. This new approach, however, required a spot size of over 30 µm.

### Analyses of abyssal peridotite orthopyroxene samples

For analyzing the hydrogen contents of the abyssal peridotite orthopyroxene samples, the SIMS determinations employed a $^{16}$O$^-$ primary ion beam operating with a 30 nA current with a total impact energy of 23 keV in Gaussian mode, providing a circa 25 µm diameter beam at the point of impact on the polished sample surface. Each analysis was preceded by a 90 s pre-sputtering using a 50 × 50 µm$^2$ raster. Prior to taking data, the raster was turned off. In order to assure that the crater was precisely centered on the field aperture, a centering scan was conducted prior to each analysis using two sets of orthogonal electrical deflection plates. To avoid hydrogen adsorbed from the residual glasses in the analysis chamber (total pressure range from 2.7 to $2.3 \times 10^{-7}$ Pa) a small field aperture of 550 × 550 µm$^2$ was used, equivalent of a field of view of only 6 × 6 µm$^2$. Thus, the field of view of the mass spectrometer was limited to the very center of the primary beam’s Gaussian distribution. The mass spectrometer was operated in dynamic mono-collection mode at a mass resolution of M/ΔM ≈ 2500 at 10 % peak height. A 150 eV wide energy bandpass was used. A single analysis consisted of 16 cycles of peak switching between $^1$H (4 seconds per cycle) and $^{30}$Si (1 s), thus a single analysis required a little over three minutes including the pre-sputtering process. All data were recorded using an ETP133H pulse counter to which deadtime correction of 46.2 ns was applied based on a delay circuit in the pre-amplifier electronics. The $^1$H/$^{30}$Si repeatability on $n = 13$ determinations spread over the two-day analytical session on our most hydrogen enriched reference material (1b-5-opx1, $249 \pm 6$ µg/g $H_2O$) was $\pm 3.2$ % (1s). The best-fit regression line for the $n = 41$ analyses conducted in total on the three RMs yielded $R^2 = 0.90$, so we infer that a linear calibration between $[H(\mu g/g)/SiO_2]$true vs. $[H^+/^{30}Si^+]$measured is reasonable. However, this regression line had a negative intercept value, equivalent to -8 µg/g $H_2O$. Since the vacuum conditions during this run were comparable to those during the calibration of the mount containing the blank, we conclude that the $H_2O$ background for these analyses was comparably low, probably in the single digit µg/g range, and therefore decided to use a linear fit forcing the calibration line through zero for the calculation of the $H_2O$ contents of the samples. We have thus not applied any further background correction, but one must bear in mind that for samples with lower hydrogen contents there may be a few µg/g background which has not been addressed and that such SIMS data might have a small systematic offset.

### Results

#### Reference orthopyroxene

**Major element compositions**

The multiple analyses per grain do not vary significantly, confirming good homogeneity for our suite of RMs. All orthopyroxene grains are enstatitic with Mg#, defined as MgO/(MgO+FeO), between 0.83 and 0.86 and Cr#, defined as Cr$_2$O$_3$/(Cr$_2$O$_3$+Al$_2$O$_3$), between 0.05 and 0.12. Mean MgO ranges from 31.4 ± 0.2 wt% (Mo22-opx2) to 32.9 ± 0.2 wt% (Mo8531-opx1), mean FeO from 5.30 ± 0.16 wt% (E-K1-opx1) to 6.58 ± 0.13 wt% (Mo21-opx1). Mean SiO$_2$ varies between 53.9 ± 0.3 wt% (1b-5-opx1) and 55.1 ± 0.2 wt% (Mo8531-opx1), mean Al$_2$O$_3$ between 4.02 ± 0.06 wt% (Mo8531-opx1) and 5.56 ± 0.06 wt% (E-K1-opx1), and mean Cr$_2$O$_3$ between 0.21 ± 0.04 wt% (Mo21-opx2) and 0.69 ± 0.02 wt% (1b-5-opx1) (Table 2).

#### FTIR spectra and water contents

The FTIR spectra of orthopyroxenes Mo21-opx1, Mo22-opx5, and 1b-5-opx1, which were used as RMs for the SIMS analyses of the samples, are shown in Fig. 2a-c. These spectra were recorded at three different locations on each grain (1, 2, 3) using both horizontal (h) and vertical (v) polarization (parallel to the minimum and maximum absorption) in three random but mutually orthogonal directions (A, B, C),
Table 2: Averaged major element compositions of the reference orthopyroxenes measured by EPMA

| Reference orthopyroxene | SiO$_2$ [wt%] | TiO$_2$ [wt%] | Al$_2$O$_3$ [wt%] | Cr$_2$O$_3$ [wt%] | FeO$^a$ [wt%] | MnO [wt%] | MgO [wt%] | NiO [wt%] | ZnO [wt%] | CaO [wt%] | Na$_2$O [wt%] | Total [wt%] | Mg$^b$ | Cr$^c$ | N |
|------------------------|--------------|---------------|-------------------|-----------------|-------------|----------|----------|----------|--------|----------|-------------|------------|-------|-------|---|
| Mo21-opx1*             | 54.90 ± 0.14 | 0.16 ± 0.01   | 4.63 ± 0.10       | 0.27 ± 0.03     | 6.58 ± 0.13  | 0.17 ± 0.03| 32.44 ± 0.19| 0.10 ± 0.02| 0.01 ± 0.02| 0.46 ± 0.06| 0.10 ± 0.01 | 99.80 ± 0.36| 0.83 ± 0.00| 0.06 ± 0.00| 8 |
| Mo21-opx2              | 54.95 ± 0.35 | 0.15 ± 0.02   | 4.38 ± 0.23       | 0.21 ± 0.04     | 6.53 ± 0.14  | 0.15 ± 0.03| 32.79 ± 0.12| 0.08 ± 0.03| 0.02 ± 0.03| 0.42 ± 0.03| 0.09 ± 0.01 | 99.78 ± 0.33| 0.83 ± 0.00| 0.05 ± 0.01| 8 |
| Mo22-opx1              | 54.35 ± 0.40 | 0.15 ± 0.02   | 5.02 ± 0.07       | 0.35 ± 0.03     | 6.23 ± 0.13  | 0.13 ± 0.03| 32.02 ± 0.13 | 0.11 ± 0.02| 0.03 ± 0.02| 0.83 ± 0.04| 0.19 ± 0.02 | 99.40 ± 0.52| 0.84 ± 0.00| 0.06 ± 0.01| 8 |
| Mo22-opx2              | 54.2 ± 0.34  | 0.17 ± 0.02   | 5.34 ± 0.12       | 0.39 ± 0.02     | 6.27 ± 0.06  | 0.15 ± 0.01| 31.42 ± 0.20 | 0.10 ± 0.03| 0.03 ± 0.03| 0.89 ± 0.04| 0.21 ± 0.01 | 99.16 ± 0.43| 0.83 ± 0.00| 0.07 ± 0.00| 8 |
| Mo22-opx3              | 54.6 ± 0.28  | 0.17 ± 0.02   | 5.05 ± 0.09       | 0.34 ± 0.02     | 6.20 ± 0.16  | 0.14 ± 0.01| 32.04 ± 0.28 | 0.11 ± 0.02| 0.01 ± 0.02| 0.87 ± 0.03| 0.20 ± 0.02 | 99.80 ± 0.57| 0.84 ± 0.00| 0.06 ± 0.00| 8 |
| Mo22-opx4              | 54.4 ± 0.22  | 0.15 ± 0.02   | 5.19 ± 0.11       | 0.37 ± 0.04     | 6.29 ± 0.06  | 0.17 ± 0.02| 31.96 ± 0.22 | 0.11 ± 0.02| 0.02 ± 0.03| 0.87 ± 0.02| 0.18 ± 0.02 | 99.79 ± 0.33| 0.84 ± 0.00| 0.07 ± 0.01| 8 |
| Mo22-opx5*             | 54.52 ± 0.22 | 0.17 ± 0.02   | 5.19 ± 0.08       | 0.37 ± 0.03     | 6.28 ± 0.09  | 0.15 ± 0.01| 31.86 ± 0.19 | 0.09 ± 0.03| 0.01 ± 0.02| 0.88 ± 0.03| 0.19 ± 0.02 | 99.71 ± 0.41| 0.84 ± 0.00| 0.07 ± 0.01| 8 |
| Mo22-opx6              | 54.51 ± 0.16 | 0.16 ± 0.02   | 5.21 ± 0.11       | 0.37 ± 0.02     | 6.30 ± 0.15  | 0.16 ± 0.03| 31.99 ± 0.09 | 0.12 ± 0.03| 0.03 ± 0.03| 0.91 ± 0.01| 0.19 ± 0.00 | 99.94 ± 0.29| 0.84 ± 0.00| 0.07 ± 0.00| 8 |
| Mo831-opx1             | 55.09 ± 0.16 | 0.17 ± 0.02   | 4.02 ± 0.06       | 0.28 ± 0.03     | 5.91 ± 0.09  | 0.14 ± 0.01| 32.93 ± 0.21 | 0.08 ± 0.02| 0.01 ± 0.01| 0.46 ± 0.03| 0.07 ± 0.02 | 99.17 ± 0.39| 0.85 ± 0.00| 0.06 ± 0.01| 6 |
| E-K1-opx1              | 54.20 ± 0.20 | 0.17 ± 0.03   | 5.56 ± 0.06       | 0.63 ± 0.02     | 5.30 ± 0.16  | 0.13 ± 0.01| 31.89 ± 0.19 | 0.09 ± 0.03| 0.03 ± 0.03| 1.17 ± 0.03| 0.19 ± 0.02 | 99.36 ± 0.39| 0.86 ± 0.00| 0.10 ± 0.00| 7 |
| 1b-5-opx1*             | 53.89 ± 0.34 | 0.08 ± 0.01   | 5.25 ± 0.10       | 0.69 ± 0.02     | 5.59 ± 0.05  | 0.14 ± 0.02| 31.94 ± 0.12 | 0.10 ± 0.02| 0.01 ± 0.01| 1.29 ± 0.02| 0.11 ± 0.01 | 99.08 ± 0.30| 0.85 ± 0.00| 0.12 ± 0.00| 6 |

N is the number of analyses

Uncertainties are reported as 1 standard deviation

$^a$FeO: all iron is treated as Fe$^{2+}$.

$^b$Mg$#$ is defined as MgO/(MgO+FeO)

$^c$Cr$#$ is defined as Cr$_2$O$_3$/(Cr$_2$O$_3$+Al$_2$O$_3$)
leading to a total of 18 spectra for one crystal. Importantly, the sets of six spectra representing the three different locations on the crystal contain the same OH bands of identical height in horizontal/vertical direction of the infrared polarizer, indicating that this material is homogenous in both its hydrogen content and in terms of the nature of the hydrogen molecular environment within the crystal. Thus, the \( \text{H}_2\text{O} \) concentrations of a single grain calculated for the three different locations are consistent.

Depending on crystal orientation, distinctive bands can be found in all samples around 3600, 3570, 3520, and 3420/3410 cm\(^{-1}\), and less prominent bands around 3300, 3210, and 3060 cm\(^{-1}\). These bands are ascribed to intrinsic OH in aluminous orthopyroxene (Beran and Zemann 1986; Skogby et al. 1990; Peslier et al. 2002; Stalder 2004). Pleochroism between the different orientations A, B, and C is variably strong since the individual grains are not oriented according to their crystallographic axes. Fig. 2d depicts
infrared spectra recorded both prior to and after dehydration of the grain Mo22-opx3. No hydrogen-bearing species are present in the dehydrated spectra. However, the different slopes and shapes of the spectra, depending on the crystal orientation, emphasize the problem of applying a proper background correction to each spectrum for calculating water contents.

Total H$_2$O concentrations of the reference orthopyroxenes measured by FTIR vary between 0 (dehydrated grain) and 249 ± 6 µg/g H$_2$O (Table 3). Within the range of uncertainty, multiple grains from one sample have the same or similar water contents: 148 ± 5 and 142 ± 4 µg/g H$_2$O for Mo21; 84 ± 4, 86 ± 3, 76 ± 5, 89 ± 5, 96 ± 3, and 77 ± 3 µg/g H$_2$O for Mo22; and 233 ± 8 and 227 ± 5 for E-K1. The good internal precision as indicated by low standard deviations is also notable.

As the range of orthopyroxene water contents from abyssal peridotites in former studies varies between 0 and 330 µg/g H$_2$O (Peslier et al. 2007; Warren and Hauri 2014; Hesse et al. 2015; Schmädicke et al. 2018) and we expect our samples from equivalent rocks to have similar contents, the selected reference minerals are well suited for use as SIMS calibration materials.

**SIMS calibration**

The subsequent SIMS determinations were calibrated using the reference orthopyroxenes that had been characterized by FTIR for their H$_2$O contents. These results are reported in Table 4. We concluded that a linear relationship exists between H$_2$O$_{(\text{wt\% FTIR})}$ vs. (1H$^+$/30Si$^+$)$_{(\text{SIMS})}$ × SiO$_2$(wt\%, EPMA$^\prime$). Therefore, the averaged measured $1H^+$/30Si$^+$ ratios are normalized by multiplication with SiO$_2$ (in wt\%, EPMA data) and plotted against the H$_2$O concentrations determined by FTIR (Fig. 3). This relationship has a slope of 2.074 × 10$^{-4}$ and a coefficient of determination of $R^2 = 0.97$. The limit of detection is <10 µg/g. In contrast to the FTIR values, where within the range of uncertainty, different orthopyroxene grains from the same sample record the same water content, the SIMS concentrations indicate that the water contents from different orthopyroxene grains of sample Mo22 are heterogenous. However, no differences between core and rim analyses could be detected in the two to five spots measured per grain, such that we assume intra-grain homogeneity.

**Abyssal peridotite orthopyroxene samples**

**Major element composition**

All orthopyroxenes from the abyssal peridotite samples are enstatites. The grains were found to be unzoned and homogeneous concerning their major element contents. The SiO$_2$ content across the eight samples varies between 53.9 ± 0.4 wt\% in sample HLY-102-D32 and 56.8 ± 0.4 wt\% in sample PS59-249-Br4 (both from Gakkel Ridge). MgO between 32.5 ± 0.5 wt\% in sample PS55-75-30 (Fram Strait) and 34.7 ± 0.4 wt\% in sample PS59-249-Br4. Mg# ranges from 0.90 to 0.92, which is typical for mantle orthopyroxene. Cr# ranges from 0.08 (HLY-102-D32) to 0.20 (PS59-249-Br4) with Al$_2$O$_3$ contents from 1.66 ± 0.16 wt\% (PS59-249-Br4) to 5.34 ± 0.31 wt\% (HLY-102-D32) and Cr$_2$O$_3$ from 0.62 ± 0.08 wt\% (PS59-249-Br4) to 0.96 ± 0.04 wt\% (PS55-75-30) (Table 5). Thus, with the exception of samples PS59-249-Br4 and HLY-102-D32, the chromium contents of the abyssal peridotite orthopyroxenes are higher than in the RMs (0.21-0.69 wt\% Cr$_2$O$_3$). The MgO contents of samples PS59-249-Br4, ODP109-670A-4R-1W, ODP125-0779A-26R-2W, and PS59-236-80-500-900 are also higher and aluminum contents of the same samples except for DSDP45-395-18R-1W-112 are lower than in the reference orthopyroxenes (31.4-32.9 wt\% MgO, and 4.02-5.56 wt\% Al$_2$O$_3$). All other elements were found to lie in the same range.

**Water contents measured by SIMS**

For eight out of twelve samples H$_2$O concentrations could successfully be quantified. The ODP304 orthopyroxenes from the Atlantis Massif and the ODP209 sample from the Mid-Atlantic Ridge are so highly altered that the indicated water contents lie far outside the calibrated range. Grain 1b-5-opx1 was used as the primary RM for the SIMS hydrogen determinations. Based on FTIR analyses this material has a hydrogen content of 249 ± 6 µg/g H$_2$O. On 13 determinations on 1b-5-opx1 a mean water content of 261 with a relative standard deviation of ± 8 % was obtained, which we believe is a reasonable estimate for the overall data quality at the higher end of our concentration range. Two other RMs, Mo21-opx1 with a nominal hydrogen content of 148 ± 5 µg/g H$_2$O and Mo22-opx5 with a nominal hydrogen content of 96 ± 3 µg/g H$_2$O via FTIR, were measured as SIMS quality control materials and to check for instrumental drift. These materials yielded concentration values of 125 ± 14 and 114 ± 6 µg/g H$_2$O, respectively (Table 6).

For reasons outlined above a calibration line forced through zero was deployed, plotting the averaged measured $1H^+$/30Si$^+$ ratios normalized by multiplication with SiO$_2$ (in wt\%, EPMA data) against the H$_2$O concentrations determined by FTIR of the reference materials contained in the sample mount. This relation has a slope of 6.62 × 10$^{-4}$ with a coefficient of determination of $R^2 = 0.99$ (Fig. 4). This calibration was used for the calculation of the water contents of the abyssal peridotite orthopyroxene samples.

The mean H$_2$O concentrations of the sample orthopyroxenes measured by SIMS range from 68 ± 7 µg/g in sample PS59-249-Br4 to 261 ± 11 µg/g in sample HLY-102-D32 (Table 6). Considering the 10 % standard deviation as a
| Reference orthopyroxene | Orientation/ polarization | Integrated absorbance area [cm$^{-2}$] | H$_2$O content [µg/g] | Orientation/ polarization | Integrated absorbance area [cm$^{-2}$] | H$_2$O content [µg/g] | Orientation/ polarization | Integrated absorbance area [cm$^{-2}$] | H$_2$O content [µg/g] |
|-------------------------|-------------------------|---------------------------------------|----------------------|-------------------------|---------------------------------------|----------------------|-------------------------|---------------------------------------|----------------------|
| **Mo21-opx1**           | A(h)-1                   | 510                                   | 35                   | B(h)-1                  | 994                                   | 68                   | C(h)-1                  | 482                                   | 33                   |
|                         | A(h)-2                   | 551                                   | 37                   | B(h)-2                  | 1058                                  | 72                   | C(h)-2                  | 527                                   | 36                   |
|                         | A(h)-3                   | 536                                   | 36                   | B(h)-3                  | 998                                   | 68                   | C(h)-3                  | 510                                   | 35                   |
|                         | A(v)-1                   | 1092                                  | 74                   | B(v)-1                  | 476                                   | 32                   | C(v)-1                  | 649                                   | 44                   |
|                         | A(v)-2                   | 1120                                  | 76                   | B(v)-2                  | 525                                   | 36                   | C(v)-2                  | 699                                   | 48                   |
|                         | A(v)-3                   | 1097                                  | 75                   | B(v)-3                  | 499                                   | 34                   | C(v)-3                  | 673                                   | 46                   |
| **Mo21-opx2**           | A(h)-1                   | 512                                   | 35                   | B(h)-1                  | 455                                   | 31                   | C(h)-1                  | 616                                   | 42                   |
|                         | A(h)-2                   | 489                                   | 33                   | B(h)-2                  | 484                                   | 33                   | C(h)-2                  | 600                                   | 41                   |
|                         | A(h)-3                   | 532                                   | 36                   | B(h)-3                  | 451                                   | 31                   |                         |                         |                     |
|                         | A(v)-1                   | 1005                                  | 68                   | B(v)-1                  | 600                                   | 41                   | C(v)-1                  | 947                                   | 64                   |
|                         | A(v)-2                   | 1007                                  | 69                   | B(v)-2                  | 630                                   | 43                   | C(v)-2                  | 985                                   | 67                   |
|                         | A(v)-3                   | 1030                                  | 70                   | B(v)-3                  | 607                                   | 41                   |                         |                         |                     |
| **Mo22-opx1**           | A(h)-1                   | 705                                   | 48                   | B(h)-1                  | 702                                   | 48                   | C(h)-1                  | 223                                   | 15                   |
|                         | A(h)-2                   | 657                                   | 45                   | B(h)-2                  | 668                                   | 45                   | C(h)-2                  | 251                                   | 17                   |
|                         | A(h)-3                   | 651                                   | 44                   | B(h)-3                  | 697                                   | 47                   | C(h)-3                  | 254                                   | 17                   |
|                         | A(v)-1                   | 250                                   | 17                   | B(v)-1                  | 255                                   | 17                   | C(v)-1                  | 386                                   | 26                   |
|                         | A(v)-2                   | 214                                   | 15                   | B(v)-2                  | 232                                   | 16                   | C(v)-2                  | 423                                   | 29                   |
|                         | A(v)-3                   | 204                                   | 14                   | B(v)-3                  | 239                                   | 16                   | C(v)-3                  | 407                                   | 28                   |
| **Mo22-opx2**           | A(h)-1                   | 390                                   | 27                   | B(h)-1                  | 288                                   | 20                   | C(h)-1                  | 581                                   | 40                   |
|                         | A(h)-2                   | 392                                   | 27                   | B(h)-2                  | 254                                   | 17                   | C(h)-2                  | 606                                   | 41                   |
|                         | A(h)-3                   | 404                                   | 28                   | B(h)-3                  | 264                                   | 18                   | C(h)-3                  | 585                                   | 40                   |
|                         | A(v)-1                   | 393                                   | 27                   | B(v)-1                  | 391                                   | 40                   | C(v)-1                  | 288                                   | 20                   |
|                         | A(v)-2                   | 395                                   | 27                   | B(v)-2                  | 531                                   | 36                   | C(v)-2                  | 305                                   | 21                   |
|                         | A(v)-3                   | 424                                   | 29                   | B(v)-3                  | 551                                   | 38                   | C(v)-3                  | 292                                   | 20                   |
| **Mo22-opx3**           | A(h)-1                   | 666                                   | 45                   | B(h)-1                  | 572                                   | 39                   | C(h)-1                  | 183                                   | 12                   |
|                         | A(h)-2                   | 757                                   | 52                   | B(h)-2                  | 621                                   | 42                   | C(h)-2                  | 207                                   | 14                   |
|                         | A(h)-3                   | 736                                   | 50                   | B(h)-3                  | 627                                   | 43                   | C(h)-3                  | 201                                   | 14                   |
|                         | A(v)-1                   | 194                                   | 13                   | B(v)-1                  | 190                                   | 13                   | C(v)-1                  | 269                                   | 18                   |
|                         | A(v)-2                   | 215                                   | 15                   | B(v)-2                  | 216                                   | 15                   | C(v)-2                  | 290                                   | 20                   |
|                         | A(v)-3                   | 223                                   | 15                   | B(v)-3                  | 214                                   | 15                   | C(v)-3                  | 285                                   | 19                   |
Table 3 (continued)

| Reference orthopyroxene | Orientation/ polarization | Integrated absorbance area [cm²] | H₂O content [µg/g] | Orientation/ polarization | Integrated absorbance area [cm²] | H₂O content [µg/g] | Orientation/ polarization | Integrated absorbance area [cm²] | H₂O content [µg/g] | Total H₂O content [µg/g] |
|-------------------------|--------------------------|----------------------------------|--------------------|--------------------------|----------------------------------|--------------------|--------------------------|----------------------------------|--------------------|--------------------------|
| Mo22-opx4               | A(h)-1                   | 538                              | 37                 | B(h)-1                   | 772                              | 53                 | C(h)-1                   | 333                              | 23                 | 89 ± 5                   |
|                         | A(h)-2                   | 568                              | 39                 | B(h)-2                   | 751                              | 51                 | C(h)-2                   | 358                              | 24                 |                         |
|                         | A(h)-3                   | 552                              | 38                 | B(h)-3                   | 716                              | 49                 | C(h)-3                   | 360                              | 25                 |                         |
|                         | A(v)-1                   | 282                              | 19                 | B(v)-1                   | 277                              | 19                 | C(v)-1                   | 356                              | 24                 |                         |
|                         | A(v)-2                   | 316                              | 22                 | B(v)-2                   | 276                              | 19                 | C(v)-2                   | 397                              | 27                 |                         |
|                         | A(v)-3                   | 299                              | 20                 | B(v)-3                   | 231                              | 16                 | C(v)-3                   | 405                              | 28                 |                         |
| Mo22-opx5*              | A(h)-1                   | 745                              | 51                 | B(h)-1                   | 729                              | 50                 | C(h)-1                   | 383                              | 26                 | 96 ± 3                   |
|                         | A(h)-2                   | 754                              | 51                 | B(h)-2                   | 710                              | 48                 | C(h)-2                   | 392                              | 27                 |                         |
|                         | A(h)-3                   | 736                              | 50                 | B(h)-3                   | 704                              | 48                 | C(h)-3                   | 365                              | 25                 |                         |
|                         | A(v)-1                   | 309                              | 21                 | B(v)-1                   | 374                              | 25                 | C(v)-1                   | 315                              | 21                 |                         |
|                         | A(v)-2                   | 316                              | 22                 | B(v)-2                   | 354                              | 24                 | C(v)-2                   | 320                              | 22                 |                         |
|                         | A(v)-3                   | 294                              | 20                 | B(v)-3                   | 335                              | 23                 | C(v)-3                   | 301                              | 21                 |                         |
| Mo22-opx6               | A(h)-1                   | 508                              | 35                 | B(h)-1                   | 260                              | 18                 | C(h)-1                   | 573                              | 39                 | 77 ± 3                   |
|                         | A(h)-2                   | 556                              | 38                 | B(h)-2                   | 257                              | 17                 | C(h)-2                   | 566                              | 39                 |                         |
|                         | A(h)-3                   | 532                              | 36                 | B(h)-3                   | 273                              | 19                 | C(h)-3                   | 577                              | 39                 |                         |
|                         | A(v)-1                   | 208                              | 14                 | B(v)-1                   | 445                              | 30                 | C(v)-1                   | 224                              | 15                 |                         |
|                         | A(v)-2                   | 236                              | 16                 | B(v)-2                   | 451                              | 31                 | C(v)-2                   | 225                              | 15                 |                         |
|                         | A(v)-3                   | 216                              | 15                 | B(v)-3                   | 470                              | 32                 | C(v)-3                   | 231                              | 16                 |                         |
| Mo8531-opx1             | A(h)-1                   | 329                              | 22                 | B(h)-1                   | 362                              | 25                 | C(h)-1                   | 390                              | 27                 | 96 ± 3                   |
|                         | A(h)-2                   | 312                              | 21                 | B(h)-2                   | 387                              | 26                 | C(h)-2                   | 404                              | 27                 |                         |
|                         | A(h)-3                   | 331                              | 23                 | B(h)-3                   | 336                              | 23                 | C(h)-3                   | 418                              | 28                 |                         |
|                         | A(v)-1                   | 590                              | 40                 | B(v)-1                   | 440                              | 30                 | C(v)-1                   | 700                              | 48                 |                         |
|                         | A(v)-2                   | 583                              | 40                 | B(v)-2                   | 458                              | 31                 | C(v)-2                   | 704                              | 48                 |                         |
|                         | A(v)-3                   | 594                              | 40                 | B(v)-3                   | 408                              | 28                 | C(v)-3                   | 682                              | 46                 |                         |
| E-K1-opx1               | A(h)-1                   | 1466                             | 100                | B(h)-1                   | 1484                             | 101                | C(h)-1                   | 1037                             | 71                 | 233 ± 8                  |
|                         | A(h)-2                   | 1462                             | 100                | B(h)-2                   | 1496                             | 102                | C(h)-2                   | 1056                             | 72                 |                         |
|                         | A(h)-3                   | 1457                             | 99                 | B(h)-3                   | 1319                             | 90                 | C(h)-3                   | 1068                             | 73                 |                         |
|                         | A(v)-1                   | 818                              | 56                 | B(v)-1                   | 979                              | 67                 | C(v)-1                   | 1143                             | 78                 |                         |
|                         | A(v)-2                   | 816                              | 56                 | B(v)-2                   | 930                              | 63                 | C(v)-2                   | 1140                             | 78                 |                         |
|                         | A(v)-3                   | 799                              | 54                 | B(v)-3                   | 871                              | 59                 | C(v)-3                   | 1183                             | 81                 |                         |
| Reference orthopyroxene | Orientation/ polarization | Integrated absorbance area [cm$^2$] | $\text{H}_2\text{O}$ content [µg/g] | Orientation/ polarization | Integrated absorbance area [cm$^2$] | $\text{H}_2\text{O}$ content [µg/g] | Orientation/ polarization | Integrated absorbance area [cm$^2$] | $\text{H}_2\text{O}$ content [µg/g] | Total $\text{H}_2\text{O}$ content [µg/g]$^a$ |
|--------------------------|--------------------------|-------------------------------------|----------------------------------|--------------------------|-------------------------------------|----------------------------------|--------------------------|-------------------------------------|----------------------------------|-----------------------------|
| E-K1-opx3                | A(h)-1                   | 1499                               | 102                              | B(h)-1                   | 1497                               | 102                              | C(h)-1                   | 79                                  | 54                              | 227 ± 5                     |
|                          | A(h)-2                   | 1525                               | 104                              | B(h)-2                   | 1517                               | 103                              | C(h)-2                   | 793                                 | 54                              |                            |
|                          | A(h)-3                   | 1507                               | 103                              | B(h)-3                   | 1514                               | 103                              | C(h)-3                   | 823                                 | 56                              |                            |
|                          | A(v)-1                   | 887                                | 60                               | B(v)-1                   | 896                                | 61                               | C(v)-1                   | 1047                                | 71                              |                            |
|                          | A(v)-2                   | 942                                | 64                               | B(v)-2                   | 924                                | 63                               | C(v)-2                   | 1067                                | 73                              |                            |
|                          | A(v)-3                   | 926                                | 63                               | B(v)-3                   | 912                                | 62                               | C(v)-3                   | 955                                 | 65                              |                            |
|                          |                         |                                    |                                  |                         |                                    |                                  |                         |                                      |                                 |                            |
| 1b-5-opx1*               | A(h)-1                   | 1916                               | 130                              | B(h)-1                   | 1789                               | 122                              | C(h)-1                   | 792                                 | 54                              | 249 ± 6                     |
|                          | A(h)-2                   | 1874                               | 128                              | B(h)-2                   | 1837                               | 125                              | C(h)-2                   | 820                                 | 56                              |                            |
|                          | A(h)-3                   | 1816                               | 124                              | B(h)-3                   | 1842                               | 125                              | C(h)-3                   | 765                                 | 52                              |                            |
|                          | A(v)-1                   | 944                                | 64                               | B(v)-1                   | 880                                | 60                               | C(v)-1                   | 1024                                | 70                              |                            |
|                          | A(v)-2                   | 916                                | 62                               | B(v)-2                   | 902                                | 61                               | C(v)-2                   | 1066                                | 73                              |                            |
|                          | A(v)-3                   | 870                                | 59                               | B(v)-3                   | 899                                | 61                               | C(v)-3                   | 1023                                | 70                              |                            |

$^a$ The grains used as RMs in the sample mount are marked with an asterisk.

$^a$ Uncertainties are reported as 1 standard deviation of the "n" reported results.
benchmark, most of the samples show little or no heterogeneity in their H₂O contents. Also, no differences in water contents between core and rim analyses could be detected. The amounts of H₂O in the samples fall close to or within the range of contents of the RMs that were characterized by FTIR.

Water contents measured by FTIR

Several orthopyroxene fragments per sample were prepared for the FTIR analyses. The refined method of crushing the highly altered abyssal peridotite samples, however, failed to provide the desired data quality: in addition to secondary amphibole bands around 3690 cm⁻¹ in many of the spectra (Skogby et al. 1990), absorption bands at ~2920 and ~2845 cm⁻¹ interfered with our measurements (Fig. 5). We attribute these bands to traces of the epoxy that was used for the preparation of the less than mm-sized specimens and is possibly trapped in microfractures due to the crushing process (Grant et al. 2007; Tollan and Hermann 2019). We noted that this contamination extends as far as in the 3400 cm⁻¹ region in our spectra, such that the contribution of the epoxy to the spectrum could not be assessed, effectively prohibiting the recovery of any meaningful information about the orthopyroxene H₂O content. Only for three grains from two samples (DSDP45-395-18R-1W-112 grains opx1 and opx4 and PS55-75-30 grain opx2) water contents could successfully be quantified. For two of these grains the water contents obtained by FTIR are significantly higher than the ones from the same samples obtained by SIMS: 100 ± 5 µg/g H₂O (SIMS) vs. 102 (+2 %) and 127 µg/g H₂O (+27 %; FTIR) for the two orthopyroxene fragments from DSDP45-395-18R-1W-112, and 206 ± 8 µg/g H₂O (SIMS) vs. 244 µg/g H₂O (+18 %; FTIR) for sample PS55-75-30 (Table 6). Whether there is a true difference between these SIMS and FTIR values or the discrepancy in these specific determinations is partially attributed to the epoxy cannot be evaluated at the present state of knowledge. However, the peridotites from both locations are highly altered, so generally one would expect the SIMS values to be higher if water-bearing alteration products were present in the analyzed sample volumes – as for example in the Atlantis Massif samples. As this is not the case, we conclude that for all other samples structurally incorporated water with little or no component derived from alteration processes was measured by SIMS.

Discussion

Water and major element contents

The orthopyroxene water contents in this study agree with H₂O concentrations of abyssal peridotite orthopyroxenes

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Table 4 SIMS data for the reference orthopyroxenes

| Reference orthopyroxene | H₂O concentration by FTIR [µg/g] | Mean ¹H⁺/³⁰Si⁺ counts measured | Mean ¹H⁺/³⁰Si⁺ counts SiO₂ content[wt.%] | H₂O concentration by SIMS [µg/g] |
|-------------------------|----------------------------------|----------------------------------|------------------------------------------|----------------------------------|
| Mo21-opx1*              | 148 ± 5                          | 5.35 x 10⁻⁴                      | 0.0294                                   | 137 ± 9                          |
| Mo21-opx2               | 142 ±4                           | 4.81 x 10⁻⁴                      | 0.0265                                   | 122 ± 2                          |
| Mo22-opx1               | 84 ± 4                           | 4.43 x 10⁻⁴                      | 0.0241                                   | 111 ± 1                          |
| Mo22-opx2               | 86 ± 3                           | 2.79 x 10⁻⁴                      | 0.0151                                   | 68 ± 3                           |
| Mo22-opx3 (dehydrated)  | 0                                | 2.35 x 10⁻³                      | 0.0013                                   | 1 ± 2                            |
| Mo22-opx4               | 89 ± 4                           | 3.14 x 10⁻⁴                      | 0.0171                                   | 78 ± 4                           |
| Mo22-opx5*              | 96 ± 3                           | 4.15 x 10⁻⁴                      | 0.0226                                   | 104 ± 2                          |
| Mo8531-opx1             | 96 ± 3                           | 4.04 x 10⁻⁴                      | 0.0222                                   | 102 ± 4                          |
| E-K1-opx1               | 233 ± 8                          | 9.98 x 10⁻⁴                      | 0.0541                                   | 256 ± 5                          |
| 1b-5-opx1*              | 249 ± 6                          | 9.45 x 10⁻⁴                      | 0.0509                                   | 241 ± 4                          |

*The grains used as RMs in the sample mount are marked with an asterisk

aUncertainties are reported as 1 standard deviation

Fig. 3 SIMS calibration line produced by all RMs presented in this study. Mo22-opx3, the dehydrated RM, is shown in grey

\[
y = \left(2.074 \cdot 10^{-4}\right)x + \left(1.028 \cdot 10^{-3}\right) \\
R^2 = 0.97
\]
Table 5  Averaged major element composition of the orthopyroxene samples from abyssal peridotites

| Sample                      | SiO$_2$ [wt%] | TiO$_2$ [wt%] | Al$_2$O$_3$ [wt%] | Cr$_2$O$_3$ [wt%] | FeO* [wt%] | MnO [wt%] | MgO [wt%] | NiO [wt%] | ZnO [wt%] | CaO [wt%] | Na$_2$O [wt%] | Total [wt%] | Mg#$^b$ | Cr#$^c$ | N     |
|-----------------------------|---------------|---------------|-------------------|-------------------|------------|-----------|-----------|-----------|-----------|-----------|----------------|-------------|--------|--------|-------|
| DSDP45-395-18R-1W-112      | 55.34 ± 0.46  | 0.05 ± 0.01   | 3.42 ± 0.17       | 0.94 ± 0.05       | 6.10 ± 0.13 | 0.14 ± 0.02 | 32.60 ± 0.43 | 0.12 ± 0.04 | 0.03 ± 0.05 | 1.64 ± 0.49 | 0.01 ± 0.01 | 100.40 ± 0.57 | 0.91 ± 0.00 | 0.16 ± 0.01 | 11    |
| PS59-249-Br4                | 56.83 ± 0.40  | 0.02 ± 0.01   | 1.66 ± 0.16       | 0.62 ± 0.08       | 5.06 ± 0.18 | 0.13 ± 0.02 | 34.71 ± 0.40 | 0.09 ± 0.03 | 0.03 ± 0.03 | 1.14 ± 0.43 | 0.01 ± 0.01 | 100.31 ± 0.44 | 0.92 ± 0.00 | 0.20 ± 0.02 | 12    |
| ODP09-670A-4R-1W            | 55.01 ± 0.46  | 0.05 ± 0.01   | 3.81 ± 0.09       | 0.83 ± 0.03       | 5.87 ± 0.11 | 0.13 ± 0.03 | 33.07 ± 0.38 | 0.10 ± 0.03 | 0.05 ± 0.06 | 1.51 ± 0.46 | 0.03 ± 0.01 | 100.47 ± 0.46 | 0.91 ± 0.00 | 0.13 ± 0.01 | 10    |
| HLY-102-D32                | 53.95 ± 0.37  | 0.07 ± 0.01   | 5.34 ± 0.31       | 0.70 ± 0.06       | 6.12 ± 0.15 | 0.14 ± 0.02 | 32.58 ± 0.54 | 0.10 ± 0.03 | 0.03 ± 0.04 | 1.20 ± 0.37 | 0.02 ± 0.01 | 100.24 ± 0.41 | 0.90 ± 0.00 | 0.08 ± 0.00 | 12    |
| ODP125-0779A-26R-2W        | 56.41 ± 0.21  | 0.01 ± 0.01   | 2.77 ± 0.13       | 0.74 ± 0.06       | 5.69 ± 0.16 | 0.14 ± 0.02 | 34.23 ± 0.31 | 0.08 ± 0.03 | 0.01 ± 0.02 | 0.70 ± 0.42 | 0.00 ± 0.01 | 100.79 ± 0.15 | 0.91 ± 0.00 | 0.15 ± 0.01 | 12    |
| PS55-75-30                 | 54.77 ± 0.78  | 0.11 ± 0.02   | 4.32 ± 0.08       | 0.96 ± 0.04       | 5.62 ± 0.20 | 0.14 ± 0.02 | 32.53 ± 0.49 | 0.11 ± 0.03 | 0.03 ± 0.03 | 1.52 ± 0.50 | 0.13 ± 0.06 | 100.23 ± 0.71 | 0.91 ± 0.00 | 0.13 ± 0.00 | 10    |
| PS59-236-80-500-900        | 55.53 ± 0.45  | 0.02 ± 0.02   | 2.97 ± 0.39       | 0.86 ± 0.10       | 5.36 ± 0.14 | 0.15 ± 0.02 | 33.75 ± 0.51 | 0.10 ± 0.04 | 0.02 ± 0.02 | 1.49 ± 0.47 | 0.03 ± 0.02 | 100.27 ± 0.56 | 0.92 ± 0.00 | 0.16 ± 0.01 | 11    |
| ME41/2-KD5-1               | 54.60 ± 0.45  | 0.04 ± 0.01   | 4.52 ± 0.20       | 0.87 ± 0.05       | 6.18 ± 0.14 | 0.16 ± 0.02 | 32.70 ± 0.27 | 0.10 ± 0.04 | 0.00 ± 0.00 | 1.46 ± 0.30 | 0.01 ± 0.01 | 100.63 ± 0.53 | 0.90 ± 0.00 | 0.11 ± 0.00 | 9     |

N is the number of analyses

Uncertainties are reported as 1 standard deviation

*FeO: all iron is treated as Fe$^{2+}$

*Mg# is defined as MgO/(MgO+FeO)

*Cr# is defined as Cr$_2$O$_3$/(Cr$_2$O$_3$+Al$_2$O$_3$)
published in other studies. Our DSDP45-395-18R-1W-112 and ODP109-670A-4W-1W samples, both from the 23°N region at the Mid-Atlantic Ridge have SIMS water contents of 100 ± 5 µg/g and 206 ± 7 µg/g, respectively. This is a wide range, however, the higher value is consistent with orthopyroxene data from ODP Leg 153 (23°20’N, Kane Transform, Mid-Atlantic Ridge), which contain 220–323 wt. ppm H2O measured by FTIR (Schmädicke et al. 2018). Leg 209 samples (15°39’ N at the MAR) in the same study range from 121–231 wt. ppm H2O. Unfortunately, we were not able to obtain a water content for our ODP209-1272A-26R-1W-60-65 sample, as the grain was too highly altered. The sample ME41/2-KD5-1 orthopyroxene from the Southern Atlantic Ocean contains 161 ± 6 µg/g H2O.

The highest water content in this study is detected in the HLY-102-D32 sample from Gakkel Ridge, which contains 261 ± 11 µg/g H2O. This is somewhat surprising since Peslier et al. (2007) measured distinctively lower water concentrations of 25–60 wt. ppm by FTIR for enstatites of PS66-238 samples dredged at the Gakkel Ridge. The orthopyroxene grains from samples PS59-249-Br4 and PS59-236-80-500-900 in this study, also from Gakkel Ridge, contain significantly less water: 68 ± 7 µg/g and 98 ± 9 µg/g, respectively. Nonetheless, the second value is still higher than in the Peslier et al. (2007) study. Warren and Hauri (2014) also examined two orthopyroxenes from Gakkel Ridge (HLY0102-4081 and PS59-235-17) in their SIMS study, which contain 99 ± 10 and 145 ± 18 wt. ppm H2O, respectively. These water contents are consistent with our PS59-236-80-500-900 sample.

The ODP125-0779A-26R-2W orthopyroxene from the Izu-Bonin-Mariana forearc region in this study contains 181 ± 10 µg/g H2O. A recent study by Gose and Schmädicke (2021) also investigated ODP Leg 125 and measured comparable orthopyroxene water contents between 122 and 363

### Table 6

| Reference orthopyroxene / sample | 1H+/30Si+ counts measured by SIMS | H2O content [µg/g] by FTIR | N | H2O content [µg/g] by FTIR |
|----------------------------------|----------------------------------|--------------------------|---|--------------------------|
| Mo21-opx1                        | 0.0015                           | 125 ± 14                 | 17| 148 ± 5                 |
| 1b-5-opx1                        | 0.0032                           | 261 ± 8                  | 13| 249 ± 6                 |
| Mo22-opx5                        | 0.0014                           | 114 ± 6                  | 11| 96 ± 3                  |
| DSDP45-395-18R-1W-112            | 0.0012                           | 100 ± 5                  | 4 | 107 ± 127               |
| PS59-249-Br4                     | 0.0008                           | 68 ± 7                   | 5 | n.a.                    |
| ODP109-670A-4W-1W                | 0.0025                           | 206 ± 7                  | 4 | n.a.                    |
| HLY-102-D32                      | 0.0032                           | 261 ± 11                 | 4 | n.a.                    |
| ODP125-U779A-26R-2W              | 0.0040                           | 181 ± 9                  | 4 | n.a.                    |
| PS55-75-30                       | 0.0025                           | 206 ± 8                  | 5 | 244                     |
| PS59-236-80-500-900              | 0.0012                           | 98 ± 9                   | 4 | n.a.                    |
| ME41/2-KD5-1                     | 0.0020                           | 161 ± 6                  | 5 | n.a.                    |

N is the number of analyses

n.a. indicates that quantification of FTIR water contents was not possible

Uncertainties are reported as 1 standard deviation

Fig. 4 SIMS calibration line for the analyses of the abyssal peridotite orthopyroxene samples produced by RMs Mo22-opx5, Mo21-opx1, and 1b-5-opx1 containing 96, 148, and 249 µg/g H2O, respectively, based on FTIR (black symbols). Water contents of the samples (colored symbols) are calculated using this calibration. Yellow symbols are used for the Arctic samples, blue for the Atlantic samples, green for the South Atlantic sample and orange for the Pacific sample with orthopyroxene data from ODP Leg 153 (23°20’N, Kane Transform, Mid-Atlantic Ridge), which contain 220–323 wt. ppm H2O measured by FTIR (Schmädicke et al. 2018). Leg 209 samples (15°39’ N at the MAR) in the same study range from 121–231 wt. ppm H2O. Unfortunately, we were not able to obtain a water content for our ODP209-1272A-26R-1W-60-65 sample, as the grain was too highly altered. The sample ME41/2-KD5-1 orthopyroxene from the Southern Atlantic Ocean contains 161 ± 6 µg/g H2O.

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wt. ppm H₂O by FTIR (average 215 wt. ppm H₂O) at Conical seamount.

In contrast to experimental data on doped crystals where correlations of water contents with major elements are evident (Rauch and Keppler 2002; Stalder and Skogby 2002; Stalder 2004; Stalder et al. 2005), correlations in natural samples are less obvious due to their greater chemical complexity. However, several studies on natural upper mantle orthopyroxene have found well-defined correlations between the mineral’s water content and its Al₂O₃, FeO, and/or MgO contents (Peslier and Bizimis 2015; Kilgore et al. 2018; Schmädicke et al. 2018; Schaffer et al. 2019; Ashley et al. 2020). The present set of samples also indicates that major element composition and SIMS determined water contents are related. Our abyssal peridotite orthopyroxene samples from diverse locations cover a broad range of Mg# and Cr# (Fig. 6a). In particular Cr# (Fig. 6c) and Al₂O₃ (Fig. 6d) correlate well with the H₂O contents measured by SIMS (\( r = -0.89 \) and 0.80, respectively). Correlation coefficients with TiO₂ (Fig. 6b), FeO (Fig. 6f) and MgO are 0.59, 0.56, and -0.55, respectively. Other major elements do not seem to be related to the amount of structural water.

**SIMS versus FTIR**

Once a calibration and analytical routine have been established, SIMS offers the advantages of being a rapid method for quantifying total hydrogen contents with the potential of analyzing targeted samples in the low nanogram mass range. In the case of abyssal peridotite, SIMS also has the major advantage of much simpler sample preparation requirements as compared to FTIR, because the latter requires the preparation of crystals in three orientations. On the other hand, a significant challenge of the SIMS technology is the need for well-characterized, matrix-matched reference materials, which ideally include a blank material. Another aspect is the need to assure exceptionally good vacuum quality in the analysis chamber, as the residual H₂O and H₂ in the chamber can be a significant source of background due to molecules adsorbed at the analysis location during the course of data acquisition. For our samples with water contents of (several) hundred µg/g H₂O a possible hydrogen background of a few µg/g H₂O was not a major concern. Koga et al. (2003) report hydrogen counts of tens of ions per second, corresponding to a blank of 2-4 µg/g H₂O, which is similar to what can be achieved with FTIR. An FTIR detection limit below ~1 µg/g H₂O is very challenging because of issues related to the optical quality of the sample, possible biases introduced by the various calibration strategies, and the method of baseline correction (Mosenfelder and Rossman 2013; Kumamoto et al. 2017). The main disadvantage of FTIR is that depending on the method (polarized measurements in three orthogonal orientations vs. non-polarized/statistical
Fig. 6 SIMS water contents as a function of major element composition determined from EPMA analyses for our set of abyssal peridotite orthopyroxene samples (colored symbols) and the new RMs in this study (black and grey symbols). a) Mg# versus Cr#, b) H_2O versus TiO_2, c) H_2O versus Cr#, d) H_2O versus Al_2O_3, e) H_2O versus Mg#, f) H_2O versus FeO. Black symbols are assigned to the three RMs used for the SIMS calibration of our sample analyses. All other RMs are shown in grey. The error bars correspond to 1 standard deviation.
measurements in only one orientation) sample preparation can easily become very time-intensive or even impossible, particularly for small or poor-quality samples such as abyssal peridotite, which usually contains only few suitable grains on thin section scale.

As spatial resolution is higher, SIMS is a reliable technique for detecting compositional zoning within a crystal. Depending on the quality of the crystal, the volume analyzed by FTIR can easily become very large (150x150x1660 µm³ in the case of the largest RM in this study, but with typical volumes of 50x50x250 µm³ for abyssal peridotite orthopyroxene grains), and one only gets an averaged value for the water content integrated over this volume. The sample volume of SIMS is smaller, often less than 10x10x1 µm³, such that zonation due to diffusional water loss/gain or compositional variation resulting from differing crystal growth events can effectively be identified and quantified.

While SIMS records total water contents, FTIR provides the significant advantage of also yielding information about hydrogen speciation, i.e. the type of substitution mechanisms, as well as possible alteration products, hydrous fluid inclusions, and secondary phases. This additional information can be essential for understanding the geological history of a sample, including such issues as thermobarometric conditions at the time of hydrogen incorporation, the assessment of redox conditions, and bulk dewatering trends brought about by high grade regional metamorphism.

### Conclusion

This study has demonstrated that when investigating pyroxenes from highly altered oceanic peridotite samples, SIMS offers significant advantages for quantifying intracrystalline H₂O contents. The SIMS sampling volume is much smaller than that offered by FTIR, allowing cracks and zones of alteration to be avoided. When SIMS analysis targets are selected carefully using optical and/or SEM imaging, water contents un-affected by alteration or inclusions can be obtained by SIMS. We observed that the water contents calculated from the SIMS analyses, although about 20% lower than the corresponding FTIR values for two samples, are similar within the range of uncertainty of the two methods, which indicates that the SIMS results do correspond to crystal bound, structural OH with little or no component derived from younger alteration processes. If this were not the case, water contents from differing localities should expectedly be much higher and scatter over a wide range of values, which is not seen in the present SIMS data.

As FTIR has the important strength of being able to distinguish between the different hydrogen species, which is needed in order to get a better understanding of the evolution of the water contents of such rocks, we suggest a combination of both methods, especially for “difficult” samples such as abyssal peridotites. We conclude that the optimal strategy combines both methods by first analyzing an individual grain by FTIR to get an overview of alteration and water content and then measure the same grain at multiple, carefully targeted locations using SIMS from which the homogeneity of the H₂O distribution can be assessed. This two-step approach provides the possibility of gaining a complete picture of the evolution of such complex materials such that implications about the geological history of the rocks can be made.

Equally important, an additional benefit of this project is that it has resulted in a set of natural reference orthopyroxenes which have been carefully cross-calibrated between FTIR (used to define the absolute hydrogen abundances) and SIMS (used to confirm micron-scale homogeneity of the hydrogen distribution). These eleven reference minerals yielding reproducible data and a SIMS limit of detection of <10 µg/g for H₂O in orthopyroxene are described in detail in this manuscript.

The water contents of orthopyroxenes from a suite of highly serpentinized abyssal peridotites from the Atlantic and Arctic Ridges as well as from the Izu-Bonin-Mariana forearc region, being difficult to impossible to analyze by FTIR, were measured using these reference orthopyroxenes according to the outlined strategy. The eight samples determined via SIMS gave water contents ranging between 68 ± 7 and 261 ± 11 µg/g H₂O, which is consistent with literature data for abyssal peridotites (see Gose and Schmädicke 2021; and references therein). All samples and reference orthopyroxenes have homogeneous water concentrations at grain scale, such that no signs of water gain or loss could be detected for either tectonically exhumed peridotites or mantle xenoliths.

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