High $H_2O$ Content in Pyroxenes of Residual Mantle Peridotites at a Mid Atlantic Ridge Segment

Pei Li$^{1*}$, Qun-Ke Xia$^{1}$, Luigi Dallai$^{2}$, Enrico Bonatti$^{3,4}$, Daniele Brunelli$^{4,5}$, Anna Cipriani$^{3,5}$ & Marco Ligi$^{4}$

Global correlations of mid-ocean-ridges basalt chemistry, axial depth and crustal thickness have been ascribed to mantle temperature variations affecting degree of melting. However, mantle $H_2O$ content and elemental composition may also play a role. How $H_2O$ is distributed in the oceanic upper mantle remains poorly constrained. We tackled this problem by determining the $H_2O$ content of orthopyroxenes (opx) and clinopyroxenes (cpx) of peridotites from a continuous lithospheric section created during 26 Ma at a 11°N Mid-Atlantic Ridge segment, and exposed along the Vema Transform.

The $H_2O$ content of opx ranges from 119 ppm to 383 ppm; that of cpx from 407 ppm to 1072 ppm. We found anomalous $H_2O$-enriched peridotites with their $H_2O$ content not correlating inversely with their degree of melting, although $H_2O$ is assumed to be incompatible during melting. Inverse correlation of $H_2O$ with Ce, another highly incompatible component, suggests post-melting $H_2O$ enrichment. We attribute a major role to post-melting temperature-dependent diffusion of hydrogen occurring above the melting region, where water-rich melt flows faster than residual peridotites through dunitic conduits cross-cutting the uprising mantle. Accordingly, estimates of the $H_2O$ content of the MORB mantle source based on $H_2O$ in abyssal peridotites can be affected by strong uncertainties.

Mantle material upwelling below mid-oceanic ridges undergoes decompression melting; the melt rises and cools to form the crust, while the melting residue forms the lithospheric mantle. It has long been held that the mantle that rises under ridges is more or less uniform in chemistry but varies in temperature by hundreds of degrees$^{1-4}$. It would follow that the correlated variability among topography, structure and composition observed along the global mid-oceanic ridge system is ultimately controlled by the temperature of the underlying mantle$^{1-4}$. However, there is growing evidence for a non-thermal influence on mantle melting processes beneath ridges, such as at Galapagos and Azores$^{5,6}$. But how volatiles, such as water, and other compositional heterogeneities, are distributed in the sub-ridge mantle, and how they affect the physical and chemical properties of mid-ocean ridges, remains poorly constrained.

An uplifted sliver of lithosphere exposed at 11°N along the Vema transform (Vema Lithospheric Section or VLS), representing a 26 Ma time interval of creation of lithosphere at a segment of Mid Atlantic Ridge (MAR), provides an opportunity to study variations through time of composition and thermal state of the sub-ridge upper mantle. Degree of melting and crustal thickness show 3–4 Ma oscillations superimposed on a long-term steady increase with time, interpreted as due to mantle thermal variations$^{8-10}$. However, radiogenic isotopes suggest that the extent of melting was also affected by mantle chemical heterogeneities$^{11,12}$.

In this study, we estimated the $H_2O$ content of nominally anhydrous minerals of the sub-ridge melting source in order to assess its potential effect on mantle melting variations. We determined the $H_2O$ content of eighteen mantle-derived abyssal peridotites recovered from ~10 closely spaced sites along the basal unit of the VLS. The crustal age of these sites, estimated from magnetic anomalies and basaltic glass $^{40}Ar/^{39}Ar$ dating, ranges from 19.2 to 10.2 Ma$^{8,11,13}$. The VLS peridotites chosen for this study have been the object of previous studies$^{8-12}$; they display protogranular/porphyroclastic textures and their relict mineral phases include orthopyroxene (opx), clinopyroxene (cpx), spinel (sp), and rare olivine$^{8-11}$; they are serpentinized to various extents$^{14}$. They are generally

1School of Earth Sciences, Zhejiang University, Hangzhou, 310027, China. 2Istituto di Geoscienze e Georisorse-CNR, Via G. Moruzzi 1, 56124, Pisa, Italy. 3Lamont-Doherty Earth Observatory of Columbia University, Palisades, New York, 10964, USA. 4Istituto di Scienze Marine-CNR, via Gobetti 101, 40129, Bologna, Italy. 5Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia, Modena, 41100, Italy. *email: peili@zju.edu.cn
similar to peridotite sampled elsewhere along ridges, considered to be residues of various extents of sub-ridge melting\textsuperscript{15}. The mineral chemistry data used here (Table 1) are from previous studies\textsuperscript{8,9,11}.

**Results**

We used infrared spectroscopy to measure the concentration of water or, more precisely, of hydroxyl (OH) defects, in both cpx and opx (see Methods). All measured pyroxene grains display several obvious absorption bands between 2800 and 3700 cm\(^{-1}\) (Supplementary Fig. 1) characteristic of the OH-stretching vibration regions in cpx and opx reported in earlier studies\textsuperscript{16-18}. The H\textsubscript{2}O content of VLS peridotites ranges from 407 to 1072 ppm in cpx and 119 to 383 ppm in opx (Table 1) and shows negligible core-rim variability (Supplementary Fig. 2). The H\textsubscript{2}O content of both cpx and opx in our samples displays weak positive or no correlation with the spinel chromium number (Cr\#) in mole fraction) (Fig. 1a), a robust index reflecting degrees of melting of the host peridotites\textsuperscript{19}. Similar results were obtained also between H\textsubscript{2}O content and other melting indices, such as Cr in pyroxene (Fig. 1b). These results are surprising because it is experimentally established and naturally observed that H\textsubscript{2}O behaves incompatibly during mantle melting, with a partition coefficient similar to that of Ce\textsuperscript{19,20}; therefore, the H\textsubscript{2}O content in melting residues is expected to decrease with degree of melting, contrary to our results. In fact, the concentration of Ce (Table 1) in the VLS peridotite pyroxenes anticorrelates with their degree of melting\textsuperscript{5}, in line with Ce being incompatible but in contrast with the behaviour of H\textsubscript{2}O (Fig. 2).

**Discussion**

In order to explain these results, we explored two alternative possibilities. One, the correlation H\textsubscript{2}O content-degree of melting in our peridotites is due to processes occurring in the sub-ridge mantle during melting. Two, it is due to processes taking place after melting. The first alternative implies a number of assumptions. One is that the pyroxene H\textsubscript{2}O content is not modified during post melting uplift of the mantle peridotites. This assumption has been shown to be valid in ODP Leg 153 peridotites drilled from the Mid Atlantic Ridge near 23\°N, where opx contain H\textsubscript{2}O in the 159-270 ppm range\textsuperscript{21}. Also favouring this assumption is our observation that H\textsubscript{2}O contents are positively correlated with a partition coefficient of 3.0 (Fig. 3), a value close to an average value of 2.6 obtained for pyroxenes in peridotites from oceanic ridges and xenoliths\textsuperscript{22}. However, if the pyroxene H\textsubscript{2}O content of the Vema mantle-derived peridotites were due to sub-ridge melting processes, we would expect elements as incompatible as H\textsubscript{2}O, i.e., Ce, Nd, Yb, etc., to behave like H\textsubscript{2}O during melting. Their concentration in pyroxenes would then correlate positively with the concentration of H\textsubscript{2}O. This is clearly not the case, as shown for instance by a plot of Nd versus H\textsubscript{2}O in the Vema cpx (Supplementary Fig. 3). Ce should also follow H\textsubscript{2}O and be higher in the depleted pyroxenes (Fig. 2). However, Ce in contrast to H\textsubscript{2}O, is lower in the depleted pyroxenes\textsuperscript{5}.

The behaviour of H\textsubscript{2}O, different from that of elements with similar partition coefficients, is hard to reconcile with the distribution of H\textsubscript{2}O in the Vema mantle peridotites being due solely to partial melting processes. Given the degrees of melting of the Vema peridotites estimated from Cr\# of spinel and pyroxenes, and given the

| Sample | Age* (Ma) | H\textsubscript{2}O (ppm) | Spinel | Opx | Cpx |
|--------|-----------|-----------------|--------|-----|-----|
| S2221-04 | 9.70 | 258 | 487 | 25.97 | 11.95 | 11.072 | 0.189 |
| S2221-05 | 9.70 | 274 | 898 | 25.97 | 12.15 | 0.065 |
| S1927-02 | 12.20 | 383 | 1005 | 24.10 | 10.79 | 0.091 |
| S1925-71 | 12.50 | 237 | 626 | 23.90 | 11.17 | 0.045 | 0.145 |
| S1925-75 | 12.50 | 615 | 1005 | 24.10 | 12.08 | 0.037 | 0.285 |
| S1924-19 | 12.80 | 201 | 529 | 17.90 | 8.85 | 0.030 | 0.400 |
| S1923-45 | 13.11 | 660 | 26.80 | 11.56 | 14.11 | 0.010 | 0.045 |
| S1923-46 | 13.11 | 335 | 944 | 25.40 | 11.22 | 10.020 | 0.110 |
| S1924-01 | 12.80 | 163 | 517 | 16.92 | 8.15 | 0.145 | 0.580 |
| VE1-1 | 13.90 | 153 | 489 | 18.60 | 10.06 | 0.372 | 1.024 |
| EW9305-15-23 | 14.07 | 305 | 1072 | 21.40 | 10.69 | 0.011 | 0.085 |
| EW9305-16-1 | 14.20 | 210 | 809 | 23.40 | 11.90 | 0.016 | 0.119 |
| EW9305-17-5 | 14.50 | 216 | 826 | 32.60 | 13.63 | 0.005 | 0.083 |
| S1904-76 | 16.10 | 304 | 1008 | 26.00 | 12.11 | 0.006 | 0.064 |
| S1904-77 | 16.10 | 220 | 629 | 25.80 | 11.89 | 0.004 | 0.043 |
| S1912-05 | 18.47 | 140 | 407 | 17.70 | 8.95 | 0.005 | 0.150 |
| S1913-03 | 18.70 | 119 | 475 | 15.80 | 9.72 | 0.036 | 0.635 |
| S1913-36 | 18.70 | 552 | 21.10 | 10.21 | 12.90 | 0.103 | 0.747 |

*Extent of melting F estimated using sp Cr# according to ref. 19.

**Table 1.** H\textsubscript{2}O contents in cpx and opx from VLS abyssal peridotites. H\textsubscript{2}O concentrations are measured by infrared spectroscopy. Melting parameters are estimated from published data\textsuperscript{8,11}. Note: Opx, orthopyroxenes; Cr#, Cr in mole fraction; (Al + Cr), in mole fraction; (Fig. 1a), a robust index reflecting degrees of melting of the host peridotites\textsuperscript{19}. Similar results were obtained also between H\textsubscript{2}O content and other melting indices, such as Ce in pyroxene (Fig. 1b).
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experimentally determined partition coefficient20,23 D melt-peridotite H2O of 0.006 to 0.012, the pre-melting H2O content of the mantle source would have to rise up to ~1,500 ppm, an unreasonably high value. Moreover, H2O behaves incompatibly during mantle melting, with a partition coefficient similar to that of Cerium24. According to the Cr# of spinel, the degree of melting of the VLS peridotites ranges from 6 to 13% (Table 1). A simple calculation predicts almost no water (less than 1 ppm) remaining in abyssal peridotites after a small (>4%) degree of fractional melting, assuming pre-melting sources25 with 200 ppm H2O and a $D_{\text{HO}}$ peridotite melt of 0.008. These additional arguments suggest that the observed water enrichment reflects post-melting hydration in the mantle.

Among post-melting processes we consider first serpentinization and contact metamorphism. The influence of serpentinization is unlikely because hydrogen diffuses sluggishly into pyroxene grains at low temperature (<300 °C) and pressure26–28. Serpentinization of the Vema peridotites at the depth of <4 km, occurred mostly near ridge axis14 at temperatures <250 °C. Our measured δ18O values ([δ18O = (18O/16O)/0.0020052-1]*1000, see Methods), range from 5.81 to 6.09‰ in opx and from 5.52 to 5.82‰ in cpx (Supplementary Table 1). Oxygen isotope fractionations between opx and cpx ($D_{\text{OPX-CPX}} = δ18O_{\text{OPX}}-δ18O_{\text{CXP}}$) range from 0.17 to 0.35, suggesting oxygen

Figure 1. Pyroxene H2O content vs extent of melting. (a) Variations of H2O content vs sp Cr# in opx and cpx from abyssal peridotites from the VLS (opx, red and cpx, orange filled circles), from ODP-Leg 153 boreholes along the Mid Atlantic Ridge21 (opx, green triangles), from Hess Deep27 (opx, dark cyan diamonds), from Southwest Indian Ridge22,28 (opx, black and cpx, gray filled square) and from Gakkel Ridge22 (opx, brown and cpx, yellow filled square). Data are listed in Supplementary Table 2. (b) H2O content in opx (red circle) and in cpx (orange circle) from the VLS peridotites vs opx Cr# and cpx Cr#, respectively.

Figure 2. H2O variability vs Ce content in cpx from VLS peridotites (orange filled circles). Black solid line indicates co-variation of H2O and Ce concentrations at increasing maximum degree of melting $F_{\text{MAX}}$. Diamonds mark $F_{\text{MAX}}$ steps of 0.5. The lack of correlation between H2O and Ce suggests post-melting H2O enrichment in the VLS residual peridotites.
The H₂O content of peridotite pyroxenes may help estimate the H₂O content of the interacting melts, thanks to the experimentally established hydrogen partition coefficients between olivine and pyroxenes (\(D_{\text{ol-cpx}}^{\text{opx-melt}} = 0.11 \pm 0.01\), \(D_{\text{ol-cpx}}^{\text{opx-melt}} = 0.08 \pm 0.01\)) and between minerals and basaltic melts (\(D_{\text{ol-cpx}}^{\text{cpx-melt}} = 0.017 \pm 0.0005\), \(D_{\text{ol-cpx}}^{\text{cpx-melt}} = 0.019 \pm 0.004\), \(D_{\text{ol-cpx}}^{\text{cpx-melt}} = 0.023 \pm 0.005\)) at upper mantle pressure (1-3 GPa) and temperature (1230–1380 °C)\(^{30,31}\). In fact, the amount of water in olivine may be determined from the water content of coexisting pyroxenes using mineral-mineral partition coefficients and the bulk water concentration for peridotite may be then estimated using mineral modes\(^{22}\) (see Methods). Accordingly, measured FTIR patterns confirm the absence of exotic H₂O in mineral alterations and fluid inclusions and show only the contribution of structural H₂O (Supplementary Figs. 1 and 2).

Low-pressure contact metamorphism can occur in the lower oceanic crust where discontinuous magma chambers are surrounded by mantle rocks. Degassing from a magma chamber can potentially refill depleted rocks by diffusion in the aureola zone. Aggregated melts differentiating in a magma chamber are characterized by high δ¹⁸O values; such a process would therefore produce a positive correlation between water content and δ¹⁸O. This is clearly not the case in the Vema peridotites, as shown in Supplementary Fig. 5.

Experimental studies of the influence of water on melting and phase assemblages in the upper mantle have shown a water content of ~200 ppm in residual nominally anhydrous minerals after incipient melting of lherzolite at the vapour-saturated solidus with pressure ranging from 2.5 to 4 GPa\(^{30–32}\). This raises the possibility that some of the investigated upper mantle peridotites may represent parcels of the upper mantle that did not go through significant melting; in fact, the maximum water contents in both pyroxenes of Vema mantle-derived peridotites resemble closely those found in these studies (~300 and 900 ppm for opx and cpx, respectively). However, mantle rocks exposed along the VLS formed originally towards the northern edge of the 80-km-long eastern MAR segment from the sub-axial melting column, which inevitably went through the melting region. Given the divergent upwelling flow of the solid mantle beneath a ridge segment, it is unlikely that off-axis mantle rocks after incipient melting may converge towards ridge axis.

One possible H₂O-rich source for post-melting enrichment of the subridge rising mantle might be H₂O-rich, low degree melts originating by off-axis incipient melting. The production of these low degree melts at the edges of the sub-ridge melting region has been hinted at by several studies\(^{21,22,27,28,30–33}\). These small quantities of H₂O-rich incipient melt may be channelled toward the axis along the sloping base of the thermal lithosphere. Distal melts trapped in the lithosphere-asthenosphere boundary may carry amounts of H₂O comparable to those we estimated in equilibrium with Vema residual pyroxenes: incipient melts from depleted upper mantle with ~200 ppm H₂O would contain about 2-3 wt% H₂O\(^{24,34}\).

Oceanic peridotites, representing fragments of the uppermost zone of the subaxial melting column, show often vein lithologies suggesting interaction with melts\(^{35–37}\). We explore the hypothesis that the H₂O rich melts recorded by our Vema residual peridotites are fractions of distal low-degree melts that migrated along lithosphere-asthenosphere boundary channels towards ridge axis (Fig. 4). These low density/low viscosity melts may tend to accumulate toward the top of the sub-ridge melting column and to react with residual peridotites before dispersing within the low-H₂O aggregate melts in sub-axial dunite channels.

The H₂O content of peridotite pyroxenes may help estimate the H₂O content of the interacting melts, thanks to the experimentally established hydrogen partition coefficients between olivine and pyroxenes (\(D_{\text{ol-px}}^{\text{opx-melt}} = 0.11 \pm 0.01\), \(D_{\text{ol-px}}^{\text{opx-melt}} = 0.08 \pm 0.01\)) and between minerals and basaltic melts (\(D_{\text{ol-melt}}^{\text{cpx-melt}} = 0.017 \pm 0.0005\), \(D_{\text{ol-melt}}^{\text{cpx-melt}} = 0.019 \pm 0.004\), \(D_{\text{ol-melt}}^{\text{cpx-melt}} = 0.023 \pm 0.005\)) at upper mantle pressure (1-3 GPa) and temperature (1230–1380 °C)\(^{30,31}\). In fact, the amount of water in olivine may be determined from the water content of coexisting pyroxenes using mineral-mineral partition coefficients and the bulk water concentration for peridotite may be then estimated using mineral modes\(^{22}\) (see Methods). Accordingly, the melt H₂O content retrieved from pyroxenes H₂O contents may range from 1.0 to 2.5 wt% (average 1.6 ± 0.4 wt%) when olivine H₂O content is estimated from opx, and from 1.0 to 3.0 wt% (average 1.8 ± 0.6 wt%) when estimated from cpx (Table 2). The differences between melt water contents estimated from opx and from cpx (Table 2) may be due to: (i) opx and/or cpx in our peridotites are not in equilibrium with the melt despite the observed equilibrium partitioning of H₂O between opx and cpx (Fig. 3); (ii) the equilibrium partition coefficients of H₂O between pyroxenes and melt determined experimentally are not appropriate because post-melting processes were not included in the experiments. In fact, experimentally determined \(D_{\text{px-melt}}^{\text{opx-melt}}\) partition coefficients for peridotite at pressures from 1 to 3 GPa range\(^{40}\) from 1.2 to 2.0, with an average of 1.5, although abyssal peridotites display

Figure 3. Co-variations of H₂O contents in cpx and opx from residual peridotites from the VLS (red filled circles), Southwest Indian Ridge\(^{22}\) (black filled square) and Gakkel Ridge\(^{22}\) (brown filled square). The dotted red line marks regression line evaluated with data from the VLS only, while the black solid line indicates a regression line including all the samples (Supplementary Table 2).
lithosphere-asthenosphere boundary (LAB) crystalizes and fractionates, increasing the melt H$_2$O content and lherzolites. Therefore, the slight positive correlation between H$_2$O content and degree of melting may simply reflect post melting metasomatic enrichment of incompatible elements, including H$_2$O, in the more refractory peridotite. Shallow mantle metasomatism should mobilize not only H$_2$O, but also LREE. However, the VLS peridotites are characterized by cpx with LREE-depleted patterns and spinel with less than 0.1 wt% TiO$_2$, indicating weak or no mantle metasomatism. Modelling based on REE and Ti-Zr in residual cpx also indicates weak re-fertilization of the residual source by small (~0.2%) amounts of partially aggregated melt. If re-fertilization was the main cause, we would expect the peridotite H$_2$O content to correlate positively with chemical indices reflecting the extent of metasomatic/melt-rock reactions such as Ce/Yb, and Na$_2$O in cpx (Supplementary Fig. 3). Absence of these correlations suggests re-fertilization is not the main cause of H$_2$O enrichment in the VLS peridotites (Supplementary Fig. 6).

Figure 4. (a) Fraction of melt (F%, colour coded) generated across the ridge segment in proximity (20 km) to the eastern Vema ridge-transform intersection. Model calculations, following method outlined by refs. 42,64, include the effect of water on the peridotite solidus. Mantle temperatures estimated by solving the steady-state advection-diffusion heat equation assuming 0°C at the seafloor and 1350°C at 150 km depth, using a three-dimensional domain of mantle flow calculations, with variable grid spacing ($512 \times 256 \times 101$), and highest grid resolution at the plate boundaries. Mantle flow velocities were estimated assuming steady-state plate-thickening passive flow beneath a ridge-transform-ridge plate boundary simulating the Vema transform geometry. Red thick dashed lines indicate boundaries between garnet and spinel stability fields. Mineral proportions in the transition zone between 85 and 60 km are assumed to vary linearly from pure garnet peridotite to pure spinel peridotite. Isotherms are indicated by thin red lines. White thick dashed line marks the region of anhydrous melting, i.e., the sub-region where water is completely exhausted from peridotite nominally anhydrous minerals. Solid thick blue line marks the upper boundary of the region that contributes to melt production (full rainbow scale), i.e. where production rate is positive. The lighter rainbow scale area marks the mantle region where a parcel of melt with a given degree of melting freezes if not extracted from the melting region, i.e., where production rate is negative. The 1100°C isotherm is assumed to approximate the lithosphere-asthenosphere boundary layer (LAB). Water-rich low degree melts, produced at the edge of the sub-ridge melting region, percolate at the base of the lithosphere (blue ellipses) where they migrate towards ridge axis. (b) Cartoon showing details of the high temperature post-melting region affected by melt flow through dunitic conduits where hydrogen may diffuse from H-rich to H-poor zones of the surrounding upper mantle. Green circles: residual peridotite minerals. Red filled vertical regions: dunitic channels.
Hydrogen diffusion into pyroxenes at mantle depths after cessation of sub ridge partial melting might have occurred in East Pacific Rise 27 (Hess Deep) and Mid Atlantic Ridge21,46,47 peridotites. H diffusion in and out of pyroxenes is favoured by high temperature. The Vema mantle peridotites have risen slowly from mantle depths after melting has stopped roughly 20 km below the seafloor (Fig. 4). The rate of ascent is similar to the half spreading rate8, i.e., ~15 mm/yr: the ascent within the mantle up to the base of the sub ridge lithosphere (~5 km below seafloor) lasts roughly 1 Ma. A good interval of this upward motion will take place at temperatures ranging from ~1250 °C to ~900 °C. During ascent of the peridotite, melts may flow in dunitic conduits and veins cross cutting the uprising mantle. The spacing of these conduits could be quite narrow48 for a nearly continuous melt extraction as we observe at the VLS. Given its high diffusion coefficient, H could diffuse from H-rich to H-depleted zones in the surrounding mantle49. The diffusion coefficient

\[ D \]

of H in pyroxene within the predicted temperature range will vary from ~1 × 10^{-18} to ~1 × 10^{-12} m^2/s, while REE diffusion coefficients are of the order of 1 × 10^{-23} m^2/s, that is, orders of magnitude lower. Thus, in 1 Ma hydrogen could travel as far as ~11 ÷ 112 m (diffusion length scale = 2√D t), while a REE would be able to travel only ~0.35 mm. This process would explain why H is decoupled from other incompatible elements in our peridotites (Supplementary Figs. 3 and 7). Higher hydrogen diffusion coefficients in cpx than that in opx would also explain why hydrogen has been mostly taken

| Sample     | \( C_{\text{H}_2\text{O}}^{\text{ol}} \) (ppm) | \( C_{\text{H}_2\text{O}}^{\text{melt}} \) (wt%) | ol | opx | cpx | sp | \( D_{\text{H}_2\text{O}}^{\text{bulk}} \) (ppm) | \( C_{\text{H}_2\text{O}}^{\text{bulk}} \) (wt%) | \( C_{\text{H}_2\text{O}}^{\text{melt}} \) (wt%) | \( C_{\text{H}_2\text{O}}^{\text{melt}} \) (wt%) |
|------------|-------------------------------|-----------------|----|----|----|----|-----------------|-----------------|-----------------|-----------------|
| S2221-04   | 28                            | 1.4             | 2.1 | 0.75 | 0.20 | 0.03 | 0.02          | 87               | 95              | 1.5             |
| S2221-05   | 30                            | 1.4             | 3.9 | 0.75 | 0.22 | 0.02 | 0.01          | 102              | 134             | 1.7             |
| S1927-02   | 42                            | 2.0             | 4.4 | 0.76 | 0.18 | 0.04 | 0.02          | 145              | 174             | 2.5             |
| S1925-71   | 26                            | 1.3             | 2.7 | 0.73 | 0.21 | 0.05 | 0.02          | 97               | 114             | 1.5             |
| S1925-75   | 49                            | 2.7             | 0.76 | 0.17 | 0.05 | 0.02 | 0.02          | 97               | 114             | 1.5             |
| S1924-19   | 22                            | 1.1             | 2.3 | 0.74 | 0.19 | 0.05 | 0.02          | 89               | 100             | 1.3             |
| S1923-45   | 53                            | 2.9             | 0.70 | 0.24 | 0.05 | 0.01 | 0.02          | 143              | 170             | 2.1             |
| S1923-46   | 37                            | 1.8             | 4.1 | 0.71 | 0.24 | 0.04 | 0.01          | 143              | 170             | 2.1             |
| S1924-01   | 18                            | 0.9             | 2.3 | 0.76 | 0.15 | 0.07 | 0.02          | 76               | 93              | 1.3             |
| VE1-1      | 17                            | 0.8             | 2.1 | 0.77 | 0.17 | 0.04 | 0.02          | 60               | 77              | 1.1             |
| EW9305-15-23 | 34                             | 1.6             | 4.7 | 0.73 | 0.21 | 0.05 | 0.02          | 102              | 132             | 1.5             |
| EW9305-16-1 | 23                              | 1.1             | 3.5 | 0.74 | 0.21 | 0.04 | 0.02          | 137              | 175             | 2.2             |
| EW9305-17-5 | 24                              | 1.1             | 3.6 | 0.71 | 0.24 | 0.04 | 0.01          | 94               | 124             | 1.5             |
| S1904-76   | 33                            | 1.6             | 4.4 | 0.69 | 0.25 | 0.05 | 0.01          | 145              | 178             | 2.1             |
| S1904-77   | 24                            | 1.2             | 2.7 | 0.70 | 0.25 | 0.04 | 0.01          | 145              | 178             | 2.1             |
| S1904-79   | 33                            | 1.8             | 1.8 | 0.77 | 0.16 | 0.05 | 0.02          | 55               | 68              | 1.0             |
| S1912-05   | 15                            | 0.7             | 2.1 | 0.75 | 0.16 | 0.06 | 0.02          | 58               | 77              | 1.0             |
| S1913-03   | 13                            | 0.6             | 2.1 | 0.75 | 0.16 | 0.06 | 0.02          | 58               | 77              | 1.0             |
| S1913-36   | 44                            | 2.4             | 0.75 | 0.18 | 0.05 | 0.02 | 0.02          | 60               | 90              | 1.0             |

Table 2. \( \text{H}_2\text{O} \) contents in olivine(ol) are estimated from opx and cpx water contents adopting mineral-mineral partition coefficients

\[ D_{\text{H}_2\text{O}}^{\text{ol}-\text{opx}} = 0.11 \] and

\[ D_{\text{H}_2\text{O}}^{\text{ol}-\text{cpx}} = 0.08 \] from refs. 38,39. Mineral modes are estimated following methods of refs. 9,59. Predicted melt water contents are calculated from opx, cpx and bulk rock water contents adopting partition coefficients

\[ D_{\text{H}_2\text{O}}^{\text{ol}-\text{melt}} = 0.0017, D_{\text{H}_2\text{O}}^{\text{opx}-\text{melt}} = 0.019 \] and

\[ D_{\text{H}_2\text{O}}^{\text{cpx}-\text{melt}} = 0.023 \] from refs. 38,39 and assuming melt in equilibrium with residual peridotites (see Methods).

Figure 5. Frequency histogram of predicted \( \text{H}_2\text{O} \) content of melts assumed in equilibrium with opx from mid ocean ridge abyssal peridotites (Supplementary Table 2). Melts global water estimates average ~1.0 ± 0.4 wt%.

H\(_2\)O contents of 439 basaltic-glasses sampled along the global mid-ocean ridge system are from the PetDB Database66 with an average water content of ~0.37 ± 0.3 wt%.

Hydrogen diffusion into pyroxenes at mantle depths after cessation of sub ridge partial melting might have occurred in East Pacific Rise27 (Hess Deep) and Mid Atlantic Ridge21,46,47 peridotites. H diffusion in and out of pyroxenes is favoured by high temperature. The Vema mantle peridotites have risen slowly from mantle depths after melting has stopped roughly 20 km below the seafloor (Fig. 4). The rate of ascent is similar to the half spreading rate8, i.e., ~15 mm/yr: the ascent within the mantle up to the base of the sub ridge lithosphere (~5 km below seafloor) lasts roughly 1 Ma. A good interval of this upward motion will take place at temperatures ranging from ~1250 °C to ~900 °C. During ascent of the peridotite, melts may flow in dunitic conduits and veins cross cutting the uprising mantle. The spacing of these conduits could be quite narrow48 for a nearly continuous melt extraction as we observe at the VLS. Given its high diffusion coefficient, H could diffuse from H-rich to H-depleted zones in the surrounding mantle49. The diffusion coefficient \( D \) of H in pyroxene within the predicted temperature range will vary from ~1 × 10^{-18} to ~1 × 10^{-12} m^2/s, while REE diffusion coefficients are of the order of 1 × 10^{-23} m^2/s, that is, orders of magnitude lower. Thus, in 1 Ma hydrogen could travel as far as ~11 ÷ 112 m (diffusion length scale = 2√D t), while a REE would be able to travel only ~0.35 mm. This process would explain why H is decoupled from other incompatible elements in our peridotites (Supplementary Figs. 3 and 7). Higher hydrogen diffusion coefficients in cpx than that in opx would also explain why hydrogen has been mostly taken
up by cpx rather than by opx, since mineral-mineral (cpx-opx) water partition coefficients recorded by our data are about twice those determined experimentally (Fig. 3). However, the hydrogen diffusion coefficients in natural opx reported in literature are of the same order of magnitude as hydrogen diffusion coefficients for diopside, although few experiments are available for natural orthopyroxenes, with total absence of hydrogen diffusion data for pure enstatite.

Diffusion of hydrogen was already suggested to explain low variability of water content relative to Ce in nominally anhydrous mantle minerals from Colorado Plateau peridotite xenoliths. However, hydrogen diffusion requires a prolonged post-melting residence time of mantle rocks at mantle conditions. The negative correlation between opx water contents and mantle equilibration temperatures observed comparing peridotites from ODP Legs 153 and 149 supports this idea, i.e., lower equilibration temperatures imply longer H diffusion times during mantle rise and consequently higher water contents. Oxygen isotopes tell here the same story. In fact, δ18O and water content for opx and cpx define a slight negative trend suggesting that at nominally zero W/R ratio, high temperature H2O diffusion may have produced a slight depletion in oxygen isotope composition. High temperature H2O incorporation occurs upon cooling according to the oxygen isotopic equilibrium fractionation in opx and cpx, that in turn depends on equilibration temperatures. This explains why opx and cpx oxygen isotope contents do not correlate positively with their H2O contents.

Our post-melting models of H2O enrichment of sub-ridge mantle peridotites do not exclude that different parcels of pre-melting mantle along the VLS may have contained different amounts of H2O, and that these different H2O contents, in addition to temperature, may have caused temporal variations of degree of melting. However, post-melting H diffusion and H2O redistribution make it difficult to reconstruct pre-melting H2O contents. If our models are correct, it would follow that, due to post melting mobility of H in the suboceanic upper mantle, estimates of the H2O content of the pre-melting mantle source of MORB based on the H2O content of abyssal peridotite pyroxenes, may be affected by strong uncertainty.

Methods

FTIR measurements of H2O content. Water content determinations followed methods of ref. Infrared measurements were carried out in 10 to 15 relatively large and clean grains of each mineral picked from the peridotites. The selected grains were mounted in a self-supporting epoxy matrix, and double polished to a thickness of ~0.2 mm. We obtained infrared unpolarized spectra at wavelengths ranging from 1250 to 4000 cm⁻¹ on a Nicolet 5700 FTIR spectrometer, coupled with a Continuum microscope at USTC, using a Kr beam-splitter and a liquid-nitrogen cooled MCT-A detector. A total of 128 scans were accumulated for each spectrum at a 4 cm⁻¹ resolution. The aperture size was set from 30 × 30 μm to 100 × 100 μm, depending on the size and quality of the mineral grains to be analyzed. Accurate determination of OH concentrations in optically anisotropic minerals requires a prolonged post-melting residence time of mantle rocks at mantle conditions. The negative correlation of OH concentrations in optically anisotropic minerals obtained by non-polarized light on unoriented grains was proven to be a reliable method both theoretically and practically. The mineral water content was calculated by the transformed Beer-Lambert law:

$$C = 3A/(I \cdot t),$$

where C is the water content of minerals in ppm, A is the non-polarised integral absorbance, I is the absorption coefficient (7.09 ppm⁻¹ cm⁻² for cpx and 14.84 ppm⁻¹ cm⁻² for opx, ref. 56) and t is the thickness in cm, measured by a digimatic indicator for each grains. The average value was used to obtain water content. Uncertainties in water contents calculated from Eq. (1) derive from: (i) using non-polarized infrared beams on non-oriented minerals (<10%); (ii) baseline correction (<5%); (iii) variable sample thickness (<3%); and (iv) differences between the absorption coefficients (<10%) of our samples and those of the samples used by ref. 37 due to differences in composition. The total uncertainty is estimated to be less than 20–30%.

Water content of melt in equilibrium with residual peridotite. The water contents of the percolating melts in equilibrium with the residual peridotites were estimated calculating bulk water concentration of peridotites using mineral modes and determining bulk H2O partition coefficient between peridotite and melt using experimentally determined partition coefficients between minerals and melt:

$$C_{H_2O}^{\text{bulk}} = \frac{C_{H_2O}^{\text{ol}} X_{\text{ol}} + C_{H_2O}^{\text{cpx}} X_{\text{cpx}} + C_{H_2O}^{\text{opx}} X_{\text{opx}}}{D_{\text{ol}}^{\text{bulk-melt}} X_{\text{ol}} + D_{\text{cpx}}^{\text{bulk-melt}} X_{\text{cpx}} + D_{\text{opx}}^{\text{bulk-melt}} X_{\text{opx}}},$$

with j = ol, cpx, opx and where $C_{H_2O}^{\text{ol}}, C_{H_2O}^{\text{cpx}}, C_{H_2O}^{\text{opx}}$ and $D_{\text{ol}}^{\text{bulk-melt}}, D_{\text{cpx}}^{\text{bulk-melt}}, D_{\text{opx}}^{\text{bulk-melt}}$ are the water contents of the melt, of the bulk peridotite and of olivine and pyroxenes; $C_{H_2O}^{\text{ol}}, C_{H_2O}^{\text{cpx}}, C_{H_2O}^{\text{opx}}$ and $D_{\text{ol}}^{\text{bulk-melt}}, D_{\text{cpx}}^{\text{bulk-melt}}, D_{\text{opx}}^{\text{bulk-melt}}$ are the partition coefficients of water between bulk peridotite and melt, and between olivine-pyroxenes and melt; and $X_j$ are the mineral abundances of olivine, cpx and opx, respectively.

The partition coefficients of water between minerals and melt are given by definition:

$$D_{H_2O}^{j-melt} = \frac{C_{H_2O}^{j}}{C_{H_2O}^{\text{bulk}}} \Rightarrow C_{H_2O}^{\text{melt}} = \frac{\sum_j C_{H_2O}^{j} X_{j}}{\sum_j D_{H_2O}^{j-melt} X_{j}} \Rightarrow C_{H_2O}^{j} = D_{H_2O}^{j-melt} \cdot C_{H_2O}^{\text{melt}}.$$

Partition coefficients of water between peridotite mineral assemblages and melt determined experimentally may depend from mineral chemistry (i.e., Al2O3), oxygen fugacity and P-T conditions. Here we assume water partition coefficients determined experimentally at upper mantle pressure (1-3 GPa) and temperature (1230–1380°C) of ref. 38 (i.e., $D_{H_2O}^{\text{bulk}} = 0.017 \pm 0.0005$, $D_{H_2O}^{\text{bulk-melt}} = 0.019 \pm 0.004$, $D_{H_2O}^{\text{bulk-melt}} = 0.023 \pm 0.005$). Assuming that the mineral phases are in equilibrium with the melt and that the adopted partition coefficients reflect exactly the
observed equilibrium, then Eqs. (2) and (3) are equivalent. Taking into account uncertainties in the mineral water content determinations and in the experimental determined partition coefficients, Eq. (3) provides different values of melt water content for each mineral phase of the residual peridotite:

$$C_{melt}(j) = \frac{C_{H_2O}^l}{D_{H_2O}^{melt}} \Rightarrow C_{H_2O}^m = D_{H_2O}^{melt} \cdot C_{melt}(j),$$

where $C_{melt}(j)$ are the melt water contents estimated from mineral phase $j$. By replacing $C_{H_2O}^l$ from Eq. (4) into Eq. (2), we obtain:

$$C_{melt} = \frac{C_{melt}(a)D_{H_2O}^{al-melt}X_{al} + C_{melt}(cpx)D_{H_2O}^{cx-melt}X_{cpx} + C_{melt}(opx)D_{H_2O}^{opx-melt}X_{opx}}{D_{H_2O}^{al-melt}X_{al} + D_{H_2O}^{cx-melt}X_{cpx} + D_{H_2O}^{opx-melt}X_{opx}}$$

$$= \frac{\sum C_{melt}(j)D_{H_2O}^{melt}X_j}{\sum D_{H_2O}^{melt}X_j} \quad \text{with} \quad w_j = D_{H_2O}^{melt}X_j \quad \text{and} \quad \sum X_j = 0$$

Equation (5) represents a weighted average of melt water contents estimated from mineral phases of the residual peridotite. The mean-value theorem states that results for $C_{melt}(j)$ are always in between the minimum and maximum value of the estimated melt water contents ($C_{H_2O}^m$) for each mineral phase compositions $X_j$, i.e.:

$$\min(C_{melt}(j)) \leq C_{melt} \leq \max(C_{melt}(j)) \quad \forall X_j.$$

Our samples contain no olivine relics. Although we were able to estimate mineral abundances in our samples following methods of refs. 60, 61 (Tab. 2), we were not able to measure any olivine water contents. Thus, olivine water contents have to be inferred from water contents of pyroxenes adopting mineral-mineral partition coefficients, i.e.:

\[
\begin{align*}
C_{H_2O}^{al} &= D_{H_2O}^{al-melt} \cdot C_{melt}^{al} = D_{H_2O}^{al-melt} \cdot \frac{C_{H_2O}^{al}}{D_{H_2O}^{melt}} = D_{H_2O}^{al-melt} \cdot C_{H_2O}^{al} \quad \text{(a)} \\
C_{H_2O}^{cpx} &= D_{H_2O}^{cx-melt} \cdot C_{melt}^{cpx} = D_{H_2O}^{cx-melt} \cdot \frac{C_{H_2O}^{cpx}}{D_{H_2O}^{melt}} = D_{H_2O}^{cx-melt} \cdot C_{H_2O}^{cpx} \quad \text{(b)}
\end{align*}
\]

where $C_{H_2O}^{al}$ and $C_{H_2O}^{cpx}$ are olivine water contents inferred from opx and cpx water contents; $D_{H_2O}^{al-melt}$ and $D_{H_2O}^{cx-melt}$ are mineral-mineral partition coefficients. Here, we adopted those of ref. 59, i.e., $D_{H_2O}^{al-melt} = 0.11 \pm 0.01$, $D_{H_2O}^{cx-melt} = 0.08 \pm 0.01$. Replacing Eq. (7) into Eq. (2) we obtain:

\[
\begin{align*}
C_{H_2O}^{melt(a)} &= \frac{C_{melt}(cpx)D_{H_2O}^{al-melt}X_{al} + C_{melt}(opx)D_{H_2O}^{cx-melt}X_{cx} + C_{melt}(al)D_{H_2O}^{opx-melt}X_{opx}}{D_{H_2O}^{al-melt}X_{al} + D_{H_2O}^{cx-melt}X_{cx} + D_{H_2O}^{opx-melt}X_{opx}} \\
C_{H_2O}^{melt(b)} &= \frac{C_{melt}(al)D_{H_2O}^{al-melt}X_{al} + C_{melt}(cpx)D_{H_2O}^{cx-melt}X_{cx} + C_{melt}(opx)D_{H_2O}^{opx-melt}X_{opx}}{D_{H_2O}^{al-melt}X_{al} + D_{H_2O}^{cx-melt}X_{cx} + D_{H_2O}^{opx-melt}X_{opx}}
\end{align*}
\]

Equation (8) and the mean-value theorem imply that the melt water content predictions $C_{H_2O}^{melt(a)}$ and $C_{H_2O}^{melt(b)}$ satisfy inequality $C_{melt(a)} \leq C_{melt} \leq C_{melt(b)}$ for each mineral phase abundances ($X_j$). These results suggest that melt water contents estimated from opx and cpx represent the lower and upper limits of water contents of melts in equilibrium with residual peridotites regardless of their mineral abundances.

**Oxygen isotopic ratios.** Following method of ref. 60, oxygen isotopes were measured at the Consiglio Nazionale delle Ricerche-Istituto di Geoscienze e Georisorse of PISA by laser fluorination 61, reacting 1 to 1.5 mg opx and cpx fragments in F2 gas 62. We irradiated the samples with a 25 W CO2 laser operating at a wavelength of 10.6 µm (ref. 63). Three pre-fluorination steps were made before running new sets of analyses in order to remove the moisture in the holder and in the line. O2 produced during laser fluorination together with excess fluorine were passed through potassium chloride salt; excess fluorine was converted into a potassium-fluoride salt and chlorine gas. A cryogenic trap cooled at liquid nitrogen temperature was then used to freeze chlorine. After purification, O2 was trapped over a cold finger filled with 5 A zeolites 60, and transferred to a Finnigan Delta Plus Mass Spectrometer for oxygen isotopic analysis. The international quartz standard NBS 30 and in-house laboratory standard Quartz Merck Standard (QMS) were measured at the beginning of each analytical session. Mineral sequences were started after the standards reached the accepted values: five to six standards were measured during each set of analyses. The average $\delta^{18}O$ value of NBS30 and QMS is 14.05 ± 0.17‰ (1σ), and 5.24 ± 0.15‰ (1σ), respectively. All $\delta^{18}O$ values are relative to SMOW (standard mean ocean water, $^{18}O/^{16}O = 2005.2 \times 10^{-6}$). At least two fragments were analyzed for each mineral, and the variations within the same sample are less than the precision of standards.
References

1. Klein, E. M. & Langmuir, C. H. Global correlations of ocean ridge basalt chemistry with axial depth and crustal thickness. *J. Geophys. Res.* 92, 8089–8115 (1987).

2. McKenzie, D. & Bickle, M. J. The Volume and Composition of Melt Generated by Extension of the Lithosphere. *J. Petrol.* 29, 625–679 (1988).

3. Langmuir, C. H., Klein, E. M. & Plank, T. In Mantle Flow and Melt Generation at Mid-Ocean Ridges vol. 71 (eds Morgan, J. P., Blackman, D. K. & Sinton, J. M.) 183–280 (American Geophysical Union, Washington DC, 1992).

4. Dalton, P. D. & Langmuir, C. H. The importance of water to oceanic mantle melting regimes. *Nature* 421, 815–820 (2003).

5. Zhou, H. Y. & Dick, H. J. Thin crust as evidence for depleted mantle supporting the Marion Rise. *Nature* 494, 195–200 (2013).

6. Orihuela, J. et al. The Vema Transverse Ridge (Central Atlantic). *Mar. Geophys. Res.* 20, 533–556 (1998).

7. Bonatti, E. *et al.* Mantle thermal pulses below the Mid-Atlantic Ridge and temporal variations in the formation of oceanic lithosphere. *Nature* 423, 499–505 (2003).

8. Aubaud, C., Hauri, E. H. & Hirschmann, M. M. Hydrogen partitioning between melt, clinopyroxene and garnet at 2 GPa in a hydrous MORB with 6 wt.% H2O. *Contrib. Mineral. Petrol.* 163, 607–625 (2008).

9. Brunelli, D., Seyler, M., Cipriani, A., Ottolini, L. & Bonatti, E. Discontinuous melt extraction and weak refertilization of mantle peridotites from the Vema Lithospheric Section (Mid Atlantic Ridge). *J. Petrol.* 47(4), 745–771 (2006).

10. Grant, K., Ingrin, J., Lorand, J. P. & Dumas, P. Water partitioning between mantle minerals from peridotites xenoliths. *Am. Mineral.* 87(3-4), 232–236 (2002).

11. Hirth, G. & Kohlstedt, D. L. Water in the oceanic upper mantle: Implications for rheology, melt extraction and the evolution of the lithosphere. *Earth Planet. Sci. Lett.* 144, 93–108 (1996).

12. Green, D. H. *et al.* Experimental study of water in nominally anhydrous minerals in the upper mantle near the water-saturated solidus. *J. Geophys. Res.* 105, 2067–2093 (2000).

13. Green, D. H. & Hauri, E. H. Partitioning of water during melting of the Earth’s upper mantle at H2O-under saturated conditions. *Earth Planet. Sci. Lett.* 248, 715–734 (2006).

14. Hauri, E. H., Gaetani, G. A. & Green, T. H. Partitioning of water during melting of the Earth’s upper mantle at H2O-under saturated conditions. *Earth Planet. Sci. Lett.* 248, 715–734 (2006).

15. Hirshmann, M. M., Tenner, T. J., Aubaud, C. & Withers, A. C. Dehydration melting of nominally anhydrous mantle: the primacy of partitioning. *Phys. Earth Planet. Inter.* 176, 54–68 (2009).

16. Ligi, M., Bonatti, E., Cipriani, A. & Ottolini, L. Water-rich basalts at mid-ocean ridge cold spots. *Nature* 410, 677–681 (2001).

17. Blackman, D. K. & Sinton, J. M. An experimental study of water in nominally anhydrous minerals in the upper mantle near the water-saturated solidus. *J. Petrol.* 35(6), 939–966 (1994).

18. Eiler, J. M. Oxygen isotope variations of basaltic lavas and upper mantle rocks. In: Valley, J. W. (Ed.), *Stable isotope geochemistry*. *Rev. Mineral Geochem.*, Mineral. Soc. Am. 43, 319–364 (2001).

19. Green, D. H. *et al.* Experimental study of the influence of water on melting and phase assemblages in the upper mantle. *J. Petrol.* 55, 2067–2096 (2014).

20. Spiegelmann, M. & Elliot, T. Consequences of melt transport for uranium series disequilibrium in young lavas. *Earth Planet. Sci. Lett.* 118, 1–20 (1993).

21. Sifre, D. *et al.* Electrical conductivity during incipient melting in the oceanic low-velocity zone. *Nature* 509, 81–85 (2014).

22. Seyler, M., Toplis, M. J., Lorand, J. P. & Ligi, M. Hydrogen partitioning between nominally anhydrous minerals and basaltic melts. *Geophys. Res. Lett.* 31(10.20611), 1–4 (2004).

23. Aubaud, C., Hauri, E. H. & Hirschmann, M. M. Hydrogen partition coefficients between nominally anhydrous minerals and basaltic melts. *Geochem. Geophys. Geosyst.* 18, 248–253 (2017).

24. Fettes, B. A., Sinton, J. M., Hauri, E. H. & Ligi, M. Experimental study of the influence of water on melting and phase assemblages in the upper mantle. *J. Petrol.* 55, 2067–2096 (2014).

25. Spiegelmann, M. & Elliot, T. Consequences of melt transport for uranium series disequilibrium in young lavas. *Earth Planet. Sci. Lett.* 118, 1–20 (1993).

26. Sifre, D. *et al.* Electrical conductivity during incipient melting in the oceanic low-velocity zone. *Nature* 509, 81–85 (2014).

27. Seyler, M., Toplis, M. J., Lorand, J. P. & Ligi, M. Hydrogen partitioning between nominally anhydrous minerals and basaltic melts. *Geochem. Geophys. Geosyst.* 18, 248–253 (2017).

28. Fettes, B. A., Sinton, J. M., Hauri, E. H. & Ligi, M. Experimental study of the influence of water on melting and phase assemblages in the upper mantle. *J. Petrol.* 55, 2067–2096 (2014).

29. Spiegelmann, M. & Elliot, T. Consequences of melt transport for uranium series disequilibrium in young lavas. *Earth Planet. Sci. Lett.* 118, 1–20 (1993).

30. Sifre, D. *et al.* Electrical conductivity during incipient melting in the oceanic low-velocity zone. *Nature* 509, 81–85 (2014).

31. Seyler, M., Toplis, M. J., Lorand, J. P. & Ligi, M. Hydrogen partitioning between nominally anhydrous minerals and basaltic melts. *Geochem. Geophys. Geosyst.* 18, 248–253 (2017).

32. Fettes, B. A., Sinton, J. M., Hauri, E. H. & Ligi, M. Experimental study of the influence of water on melting and phase assemblages in the upper mantle. *J. Petrol.* 55, 2067–2096 (2014).

33. Spiegelmann, M. & Elliot, T. Consequences of melt transport for uranium series disequilibrium in young lavas. *Earth Planet. Sci. Lett.* 118, 1–20 (1993).
42. Katz, R. E., Spiegelman, M. & Langmuir, C. H. A new parameterization of hydrous mantle melting. *Geochim. Geophys. Geosyst.* **4**, 1073 (2003).
43. Danyshevsky, L. V. The effect of small amounts of H2O on crystallization of mid-ocean ridge and backarc basin magmas. *J. Volcanol. Geotherm. Res.* **110**, 265–280 (2001).
44. Keller, T., Katz, R. E. & Hirschmann, M. M. Volatiles beneath mid-ocean ridges: Deep melting, channelised transport, focusing, and metasomatism. *Earth Planet. Sci. Lett.* **464**, 53–68 (2017).
45. Frey, F. A. & Green, D. H. The mineralogy, geochemistry and origin of lherzolite inclusions in Victorian basalites. *Geochim. Cosmochim. Acta* **38**, 1023–1059 (1974).
46. Schmädicke, E., Gose, J. & Will, T. M. Heterogeneous mantle underneath the North Atlantic: Evidence from water in orthopyroxene, mineral composition and equilibrium conditions of spinel peridotite from different locations at the Mid-Atlantic Ridge. *Lithos* **125**, 308–320 (2011).
47. Schmädicke, E., Gose, J. & Stalder, R. Water in abyssal peridotites: why are melt-depleted rocks so water rich? *Geochim. Geophys. Geosyst.* **19**, 1824–1843 (2018).
48. Kelemen, P. B., Braun, M. & Hirth, G. Spatial distribution of melt conduits in the mantle beneath oceanic spreading ridges: Observations from Ingalls and Oman ophiolites. *Geochim. Geophys. Geosyst.* **1**, 1005 (2000).
49. Marshall, E. W., Lassiter, J. C. & Barnes, J. D. On the (mis) behavior of water in the mantle: Controls on nominally anhydrous mineral water content in mantle peridotites. *Earth Planet. Sci. Lett.* **499**, 219–229 (2018).
50. Stalder, R. & Skogby, H. Hydrogen diffusion in natural and synthetic orthopyroxene. *Phys. Chem. Miner.* **30**, 12–19 (2003).
51. Hercule, S. & Ingrin, J. Hydrogen in diopside: diffusion, kinetics of extraction-incorporation, and solubility. *Am. Mineral.* **84**, 1577–1587 (1999).
52. Farver, J. R. Oxygen and Hydrogen Diffusion in Minerals. *Rev. Mineralogy & Geochem.* **72**, 447–507 (2010).
53. Li, P., Scott, J. M., Liu, J. & Xia, Q. Lateral H2O variation in the Zeaolandia lithospheric mantle controls oxygen width. *Earth Planet. Sci. Lett.* **502**, 200–209 (2018).
54. Sambridge, M., Fitz Gerald, J. D., Kovács, I., O’Neill, H. St. C. & Hermann, J. Quantitative IR spectroscopy with unpolarized light, Part I: Physical and mathematical development. *Am. Mineralogist* **93**, 751–764 (2008).
55. Kovács, I. et al. Quantitative absorbance spectroscopy with unpolarized light, Part II: Experimental evaluation and development of a protocol for quantitative analysis of mineral IR spectra. *Am. Mineralogist* **93**, 765–778 (2008).
56. Libowitzky, E. & Rossman, G. R. Principles of quantitative absorbance measurements in anisotropic crystals. *Phys. Chem. Miner.* **23**, 319–327 (1996).
57. Bell, D. R., Ihinger, P. D. & Rossman, G. R. Quantitative analysis of trace OH in garnet and pyroxenes. *Am. Mineral.* **80**, 465–474 (1995).
58. Langmuir, C. H., Klein, E. M. & Plank, T. In Mantle Flow and Melt Generation at Mid-Ocean Ridges (eds Phipps Morgan, J., Blackman, D. K. & Sinton, J. M.) 183–280 (Geophysical Monograph 71, American Geophysical Union, Washington D.C., 1992).
59. Ligi, M., Bonatti, E., Cuffaro M. & Brunelli, D. Post-Mesozoic rapid increase of seawater Mg/Ca due to enhanced mantle-seawater interaction. *Scientific Reports* **3**, https://doi.org/10.1038/srep02752 (2013).
60. Hao, Y., Xia, Q., Dallai, L. & Coltorti, M. Recycled oceanic crust-derived fluids in the lithospheric mantle of eastern China: constraints from oxygen isotope compositions of peridotite xenoliths. *Lithos* **228-229**, 55–61 (2015).
61. Sharp, Z. D. A laser-based microanalytical method for the in situ determination of oxygen isotope ratios of silicates and oxides. *Geochim. Cosmochim. Acta* **54**, 1353–1357 (1990).
62. Asprey, L. B. The preparation of very pure fluorine gas. *J. Fluori. Chem.* **7**(1), 359–361 (1976).
63. Sharp, Z. D. Oxygen isotope geochemistry of the Al2SiO5 polymorphs. *J. Fluori. Chem.* **7**(1), 359–361 (1976).
64. Ligi, M., Cuffaro, M., Chierici, F. & Calafato, A. Three-dimensional passive mantle flow beneath mid-ocean ridges: an analytical approach. *Phys. J. Int.* **175**, 783–805 (2008).
65. Niu, Y. & Green, D. H. The petrological control on the lithosphere-asthenosphere boundary (LAB) beneath ocean basins. *Earth-Science Rev.* **185**, 301–307 (2018).
66. Lehnert, K., Su, Y., Langmuir, C. H., Sarbas, B. & Nohl, U. A global geo-chemical database structure for rocks. *Geochim. Geophys. Geosyst.* **1**, 1012 (2000).

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Author contributions
P.L. developed the ideas and the methods for this study. P.L. and M.L. wrote the manuscript with input from Q.-K.X., E.B., D.B., A.C. and L.D. P.L. carried out the FTIR measurements and L.D. the oxygen isotopic analysis. All the authors discussed extensively the results and the interpretations.

Competing interests
The authors declare no competing interests.

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