The hydrogen isotopic composition and water content of southern Pacific MORB: A reassessment of the D/H ratio of the depleted mantle reservoir

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1. Introduction

Based on the pioneer work of Kyser and O’Neil (1984), the isotopic composition of hydrogen in the convective mantle is commonly assumed to be characterized by a δD of −80 ± 10‰ compared to SMOW. The D/H variations were attributed to secondary processes, especially contamination by seawater and seawater-derived fluids, both with higher δD than the mantle. In any given area, the value most likely to characterize mantle hydrogen would be the lowest observed, typically −80‰. Studies (Poreda et al., 1986; Kingsley et al., 2002; Pineau et al., 2004) have however shown co variations between δD values (ranging from −80 to −40‰) and tracers of mantle source heterogeneities (either ratios of rare-earth elements or Pb isotopes), demonstrating that source heterogeneity rather than contamination is the main factor controlling the variations of δD and H2O in MORB, OIB and seamount chain basalts. This is also consistent with studies of water to light rare-earth element ratios of similar incompatibilities (Michael, 1995; Kent et al., 1999b; Danyushevsky et al., 2000; Le Roux et al., 2006), which showed that MORB H2O/Ce (or /La) are regionally homogeneous and characteristic of the local MORB mantle source. How δD values may vary remains however typically unaddressed (except for Kingsley et al., 2002). Moreover, a recent study has shown that extracting water by induction heating of basaltic glasses in a Pt crucible (which was the preferred method in the 80’s; Kyser and O’Neil, 1984) can lower the measured δD by more than 10‰ (Clog et al., 2012). It further illustrates the need to re-evaluate the hydrogen isotopic composition of the mantle and its variability.

In the present study we re-investigate the current consensus that the δD value of the MORB mantle is equal to −80‰ and propose that a value of ≈−60‰ is more appropriate.

2. Samples locality background and analytical techniques

The Pacific–Antarctic ridge is ideal to re-investigate the D/H composition of the depleted upper mantle. Two large supersegments (from 65 to 56°S and from 52 to 41°S, sampled respectively by the French missions PACANTARCTIC 1 (1996) and 2 (2005)) present MORB compositions characterizing a rather homogeneous mantle devoid of hotspot influence (see Vlastélic et al., 2000 for the southern one; Moreira et al., 2008 and Hamelin et al., 2010 for the northern one). They are separated by a region with several fracture zones which record interactions with the Louisville hotspot, as illustrated by the greater variability of MORB compositions in radiogenic isotope ratios (Castillo et al., 1998; Géli et al., 1998; Vlastélic et al., 1998; Hamelin et al., 2011).
showed that the variations in Sr, Nd, Hf and He isotope ratios along those two supersegments result from mixing of a small, but gradually greater northwards, amount of HIMU component in the source. Most of the basalts dredged in the area are N-MORB, but there is a latitudinal trend with more enriched samples in the northern part of the sampling area.

Except for helium analyses (Moreira et al., 2008; Hamelin et al., 2011), which show homogeneous isotopic composition typical of the depleted mantle ($R/R_0 = 7.29 \pm 0.19$), there has been no study of volatile elements in this region. Moreira et al. (2008) also noted limited variations and in particular that the northern supersegment is the most homogeneous ridge portion studied with respect to He isotopic compositions.

The variations in structure and spreading rate in this area are also of importance. The spreading rate increases northwards, from 54 mm/yr at 70°S to 111 mm/yr at 40°S (DeMets et al., 1990) and is associated with a change in the structure of the ridge in the southern supersegment, from a central valley typical of slow-spreading ridges to a central dome typical of faster ridges. As noted by Vlastelíc et al. (2000), the morphology appears to be primarily controlled by the spreading rate, rather than by the mantle potential temperature. On the whole northern supersegment, the structure is typical of a fast-spreading ridge (Klingelhoefer et al., 2006; Hamelin et al., 2010). Faster ridges have typically more important and widespread hydrothermal circulation, leading to more pronounced chlorine contamination (Michael and Cornell, 1998; Bonifacie et al., 2008). Therefore, for water studies, the structure of the ridge could also be of importance, particularly in assessing the effect of contamination of seawater-derived fluids on δD values.

2.1. Sample suite

All samples in this study are glassy rims of pillow lavas dredged at the axis of the ridge, at depths between 1500 and 2800 m below sea level, except PAC1 CV07 which was dredged on an off-axis seamount (Fig. 1).

Forty basalts were analyzed for water and chlorine contents, and for δD. All the samples are N-MORB (La/Sm$_N < 1$, where $N$ marks normalization to the primitive mantle; McDonough and Sun, 1995), with a slightly higher alkali content for samples collected near the Menard Transform Fault Fracture (samples PAC2 DR7 and PAC2 DR20) due to greater extents of crystal fractionation. Most samples were previously analyzed for their compositions in major ($n = 37$), trace ($n = 35$) and radiogenic (Sr, Nd, Pb) elements isotopic compositions ($n = 37$) and some ($n = 16$) for helium concentrations and isotopic compositions (supplementary Tables 1 and 2; Vlastelíc et al., 1999, 2000; Moreira et al., 2008; Hamelin et al., 2010, 2011). We report new cerium data measured by NAA (Neutron Activation Analysis) for the samples of the southern supersegment, with the same technique as used for La and Sm by Vlastelíc et al. (2000). Supplementary Tables 3 and 4 report the δD, H$_2$O, Cl and Ce concentrations, along with geographic coordinates and depth of collection.

2.2. Water content and δD measurements

The technique used in this study has been described in Clog et al. (2012) and is summarized here. It is based on the original method described by Vennemann and O’Neil (1993). Glass samples were crushed to shards of 100 to 250 μm, washed in distilled water, ultrasonically cleaned and dried. Most of the plagioclase, olivine and altered grains were discarded using a Frantz magnetic sorting apparatus. Remaining minerals and altered chips were removed by careful handpicking under a binocular, to select only fresh glass shards.

The mass of sample typically used was 350 mg for each analysis. The sample was introduced into a pre-cleaned sealed quartz tube (2 h at 1150°C) connected to a vacuum line and heated to 250°C for half an hour to eliminate any adsorbed water. Then the samples were heated to 950°C for 45 min under a pressure of 400 Pa of pure O$_2$ obtained by thermal decomposition of CuO. The released CO$_2$ and H$_2$O (and other condensable gases such as SO$_2$) are held in a cold trap at $-196$°C (liquid nitrogen) and separated by setting the temperature at $-140$°C to keep only H$_2$O, while incondensable gases and CO$_2$ are pumped out of the line. Water is then reduced on hot uranium furnace held at 800°C to obtain H$_2$ (Bigeleisen et al., 1952). The amount of gas is measured by manometry and it is then concentrated into a sampling tube with a Toepler pump. The gas is analyzed with a dual-inlet mass spec-
trometer (Delta Plus XP). The typical reproducibility on the measurements was ±5% for water content and ±3% for δD (both 2σ, as established from the 10 analysis of the PAC2 DR20-1-1 sample). Procedural blanks amount to ≈0.4 μmol. Re-heating a sample that had previously been heated to 900°C for half an hour produced amounts of water equal to the value of our experimental blanks, demonstrating that we reached quantitative water recovery.

The uranium furnace was calibrated with three standard waters: ROSS (δD = −114.9‰), EPB-5 (δD = −44.4‰) and ORSMOW (δD = +2.4‰). These in-house standards were obtained from the LSCE (Laboratoire des Sciences du Climat et l’Environnement, Saclay, France) where they are regularly calibrated against IAEA NBS-30. We obtain an average value of δD = +0.6‰, as determined on an olivine standard and the re-produced using a scapolite standard (Cl content 4.04 wt%). Ten points were obtained on eight samples across a transsect, avoiding visible cracks or imperfection in the polished surface. The detection limit is 13 ppm, as determined on an olivine standard and the reproducibility in chlorine concentration range from 10 to 20 ppm (2σ).

3. Results

3.1. Water concentrations

Water concentrations range from 840 to 7800 ppm (n = 40), which is within the typical range for MORB (2300−3500 ppm, PetDB database: Lehnert et al., 2000; Kyser and O’Neil, 1984; Poreda et al., 1986; Jambon and Zimmermann, 1990; Pineau and Javoy, 1994; Michael, 1995; Dixon et al., 2002; Pineau et al., 2004; Le Roux et al., 2006). High water samples are rare, with only four having more than 4000 ppm H2O (supplementary Tables 3 and 4, Fig. 2b). H2O/Cl ratios range from 112 to 254 (Fig. 3a, 186 ± 30 on the southern supersegment and 173 ± 15 on the northern supersegment), within the range observed in MORB (from 100 to 350; Michael, 1995). The typical range for Pacific MORB is 180 ± 30 (Michael, 1995; Le Roux et al., 2006), and only samples south of 63°S present H2O/Cl ratios outside this range. Note that when we exclude those samples, the average on the southern supersegment stays the same. In order to better constraint the observed difference, we applied a Student’s t-test which indicated that the two H2O/Cl ratio distributions are statistically distinct (Student’s t-test, t = 2.33, df = 31, p < 0.05).

No systematic variation of water content or H2O/Cl with latitude was found (Fig. 2).

3.2. Hydrogen isotopic compositions

δD range from −76 to −48‰ (supplementary Tables 3 and 4, Fig. 2a), within the range of previously studied MORB (from −92 to −44‰; Kyser and O’Neil, 1984; Poreda et al., 1986; Chaussidon et al., 1991; Pineau and Javoy, 1994; Kingsley et al., 2002; Pineau et al., 2004; Hauri et al., 2006; Cartigny et al., 2008). The δD values show no significant correlation to either water contents or water to cerium ratios. It is however worth noting that >90% of the N-MORB from the North Pacific and Atlantic previously published have δD between −85 and −65‰ (Kyser and O’Neil, 1984; Pineau et al., 2004; Hauri et al., 2006; Cartigny et al., 2008). The values measured here are thus more comparable to previously analyzed E-MORB from other oceanic basins (Poreda et al., 1986; Kingsley et al., 2002), though N-MORB from the East Pacific Rise near 22°N and the west rift of the Easter microplate have δD close to −65‰ (Kingsley et al., 2002). There is also no correlation with Sr, Nd, Hf, Pb or He isotope data on these samples (Fig. 3b) or with the La/Sr ratio. We applied the same statistical tests to the δD data. The difference between the southern supersegment (δD = −63 ± 7‰) and the northern supersegment (δD = −58 ± 4‰) is statistically significant (Student’s t-test, t = 2.77, df = 38, p < 0.05). This holds true is the samples south of 63°S are excluded (Student’s t-test, t = 2.24, df = 32, p < 0.05).

3.3. Chlorine concentrations

Cl concentrations vary from 29 to 2400 ppm (Fig. 3c), within the MORB range (from 10 below the detection level) to more than 4000 ppm (Jambon et al., 1995; Michael and Cornell, 1998; Soule et al., 2006), 90% of measured MORB falling below 800 ppm (PetDB database)). On average, samples from the northern supersegment, where the spreading rate is higher, have higher Cl/K than samples from the southern supersegment (modes of 0.32 ± 0.58 and 0.16 ± 0.22, respectively). Average and standard deviation are calculated from the log-normal distribution adjusted to the data to account for the pronounced skew, see also Fig. 3d). Potassium and chlorine having similar bulk partition coefficient during partial melting and crystal fractionation (Michael and Cornell, 1998), the variations are thus too large to depend only upon variations in igneous processes, but reflect contamination or assimilation, as discussed in the next section.
Fig. 3. From top to bottom: H$_2$O/Ce, $^{208}$Pb/$^{204}$Pb, Cl content and Cl/K along the sampling area. Except south of Saint-Exupery fracture zone, all H$_2$O/Ce ratio are in the range of North Pacific basalts.

4. Discussion

4.1. Degassing

Contrary to CO$_2$ which can degas at high pressure, water is much more soluble in silicate melts and typically remains undersaturated in typical MORB settings (e.g., Dixon and Stolper, 1995; Jendrzejewski et al., 1996). Kyser and O’Neil (1984) suggested that loss of hydrogen could occur either as degassing of H$_2$ or CH$_4$. Subsequent studies have actually shown that MORB are more oxidized than was originally thought (Bézos and Humler, 2005; Kelley and Cottrell, 2009), and therefore, H$_2$/CH$_4$ degassing is not significant. Furthermore, all samples present very low vesicularity (<1%), are under-saturated with respect to water (Fig. 4), and can be calculated to be in equilibrium with a gas phase containing less than 5% of water for all 4 of the samples. The sample PAC1 DR10-1 is in equilibrium with a vapor phase containing more than 20% of water, and is thus the most likely to have experienced some degassing. However, its $\delta^D$ is indistinguishable from the $\delta^D$ of the sample PAC1 DR10-2 which comes from the same dredge and argues against any significant degassing-induced change in $\delta^D$ values. The homogeneity of the H$_2$O/Ce ratios observed along the supersegments is also a compelling argument against degassing. Degassing of water thus appears negligible for all of our samples.

Fig. 4. Water content as a function of eruption pressure. The lines illustrate, for a given water content and pressure, the composition of a CO$_2$–H$_2$O vapor in equilibrium, with the number being the molar percentage of H$_2$O of the vapor. All but sample PAC1 DR10-1 were unlikely to be affected by degassing.

4.2. Effects of contamination on volatile contents

It should be first noted that previous studies established that variations in major and trace elements in this sample suite are mostly due to crystal fractionation (Vlastélic et al., 2000; Hamelin et al., 2010). This is also illustrated by the evolution of La and Ce content with MgO wt% (Figs. 5a and 5b). In this section we investigate to what extent are non-igneous processes responsible for variations in water and chlorine content.

Ratios of Cl and H$_2$O to elements of similar incompatibilities (typically K, La or Ce) can be used to quantify the degree of interaction with brines or hydrated rocks during ascent (e.g., Michael, 1995; Michael and Cornell, 1998). This is because contamination of lavas by seawater-derived fluids results in an increase in chlorine content, while water content appears comparatively less (or not) affected (Michael and Cornell, 1998; Kent et al., 1999a, 1999b; Dixon and Clague, 2001; Soule et al., 2006).

Constraining the interaction with brines or hydrated rock on the basis of the $\delta^D$ alone is difficult, as the isotopic composition of the brines deep in the crust is unconstrained, while hydrated rocks can have $\delta^D$ similar to those measured in our samples (e.g., Agrinier et al., 1995). It is worth noting that experiments led to the suggestion that high-Cl brines should be depleted in D, with $\Delta^D_{vapor-brine}$ fractionation between 2 and 8‰ according to Berndt et al. (1996), but the same study also highlighted the difficulty in trying to relate the measured fractionation and the $\delta^D$ of outwards fluxes at hydrothermal vents due to uncertainties in mixing processes, temperature of the reaction, closed versus open system consideration and concurrent processes of interaction with the crustal rocks. In summary, from available studies, the D/H ratio of brines is still difficult to anticipate. Yet, it should also be noted that contamination by either brines or hydrothermally altered rocks cannot buffer the $\delta^D$ of our samples as they are all under-saturated with respect to water.

In the following discussion, we therefore focus on the H$_2$O/Ce and Cl/K ratios.
4.2.1. H₂O/Ce ratios

Water content increases smoothly with decreasing MgO wt% (Fig. 5c), suggesting that water content is primarily controlled by igneous processes rather than contamination. We also observed that the H₂O/Ce ratios are rather homogeneous on our sample suite. For our sample suite, the incompatibility of water is closer to that of Ce rather than of La, as illustrated in Fig. 6. This justifies the choice of Ce for the normalization for our sample suite. Considering the range of (La/Sm)ᵣ observed here, our results contrasts with those of Danyushevsky et al. (2000) which suggested that La should be more appropriate.

The average H₂O/Ce ratio is ≈185 ± 30 on the southern supersegment and ≈175 ± 15 on the northern one, which is, within this small range, the opposite of what would be expected from the relationship between ridge structure and degree of assimilation (Michael and Cornell, 1998). All this evidence is consistent with hydrogen contamination being a minor process whose maximum impact is negligible with respect to other processes and potential source heterogeneities (see also Fig. 7).

4.2.2. Cl/K ratios

Contrary to water, the chlorine content variations cannot be explained solely by crystal fractionation (Fig. 5d). We observe that the majority of samples that have incurred a greater extent of crystal fractionation (MgO < 7.5 wt%) have Cl content much higher than the crystal fractionation trend, which contrasts with samples with MgO > 8.0 wt%. Cl/K ratios are also higher in the northern supersegment (modes 0.32±0.09 in the northern supersegment and 0.16±0.22 in the southern supersegment, Fig. 3d), which points to more intense contamination with an increasing spreading rate, as has been proposed by Michael and Cornell (1998) and Bonifacie et al. (2008). It should be noted that this difference is however mostly driven by a couple of extremely Cl-enriched samples (PAC2 DR34-1 and PAC2 DR28-2).

A recent study (Kendrick et al., 2012), based on a global compilation of Cl and K concentrations, has proposed that the average Cl/K of uncontaminated MORB is close to 0.08. When comparing to modes of 0.16 and 0.32 on respectively the southern and northern supersegments, this would indicate that our samples are extensively contaminated with respect to Cl. Conversely, the lowest Cl/K measured on our samples are, for both segments, ≈0.03, illustrating the non-uniformity of the contamination. This would imply, for chlorine budget, that the details of the ascent and eruption scenarios are at least of equal importance to the spreading rate. Lowest Cl/K were observed in both cases where the magmatic activity is less vigorous: a near-axis seamount in the south
Fig. 7. (a) Cl/H₂O versus Ce/H₂O and curves resulting from the addition of seawater, brines with various concentrations or a serpentine with 10 wt% H₂O, 1000 ppm Cl and 10 ppm Ce to a typical uncontaminated MORB composition (2000 ppm H₂O, H₂O/Ce = 180, 1000 ppm K, 30 ppm Cl, 10 ppm Ce). (b) H₂O/Ce versus Cl/K and the same curves in this space. Those figures illustrate that the observed variations are not compatible with the addition of diluted brines, seawater or hydrated mafic rock. Shaded outlines illustrate the dispersion of the data in the southern (continuous outline) and the northern (dotted outline) supersegments.

and a sample from the S2 segment, whose structure is described as poorly defined (Hamelin et al., 2010) due to interaction with the Menard Fracture Zone in the north. Assuming that the smallest Cl/K measured correspond to uncontaminated samples rather than the higher value proposed by Kendrick et al. (2012), we conclude that more than 80% of Cl comes from contamination in our sample suites.

The contrast between the behavior of water and chlorine suggests that contamination in our sample suite is not due to assimilation of hydrated wall-rock or contribution from seawater or diluted brines, but due to either very concentrated brines or pure halite left in the crust by hydrothermal circulation (Fig. 7). It should also be noted that samples with low Cl content (<100 ppm, 12 samples) or low Cl/K (<1.6, 12 samples) present a range of δD from −76 to −51 ‰, and an average δD of −63 ‰. Those values are close to those observed for the complete sample suite (δD from −75 to −48 ‰ and δD ≈ −61 ‰). This is consistent with a very minor effect of contamination on the D/H ratio of our samples.

4.3. Crystal fractionation and partial melting effects

We calculated the water content of the source by correcting to 8% of MgO (Weaver and Langmuir, 1990; Kelley et al., 2006) and using a simple batch melting model, assuming a constant Na content of the source. The results are illustrated in Fig. 8, whose caption contains the details of the calculation.

For most (>80%) of the samples, the calculated water content is in the range 150–250 ppm. The obvious limitations of this method are the assumed homogeneity of Na content and the variations of solidus temperature with water content. In retrospect, the influence of the latter is negligible considering the limited range of calculated H₂O_source. The variations observed in water content are thus consistent with a source containing 200 ± 50 ppm of water with an extent of melting between 8 and 10%, followed by various extents of crystal fractionation.

Despite the relative homogeneity of our sample suite, we discuss in the next section the consequence of melting a possibly heterogeneous mantle source in terms of δD variability.
source with high \((\text{La}/\text{Sm})_N\). \(\delta D\) and \(\text{H}_2\text{O}\) content can be inferred, in contrast with observations near Iceland (Poreda et al., 1986) or along the Salas y Gomez seamount chain (Kingsley et al., 2002). This suggests that the heterogeneity in water contents and \(\delta D\) relates to a distinct process, and the lack of relationship with Pb isotopes (seen as a tracer for a HIMU-type component) precludes the use of the \(\delta D\) variability to constrain the D/H ratio of the HIMU component.

The only apparent relationship is a negative correlation between \(\delta D\) and \(\text{TiO}_2/\text{H}_2\text{O}\) ratios (Fig. 9c), driven by two samples from the area south of the Saint-Exupery fracture zone (PAC1 CV04 and PAC1 CV07). These two samples have the lowest \(\text{H}_2\text{O}/\text{Ce}\) of the sample suite (134 and 112), the lowest calculated \(\text{H}_2\text{O}\) source and low \(\delta D\) (−76.6 and −69.6‰). Interestingly, their \(\text{H}_2\text{O}/\text{TiO}_2\) and \(\text{K}_2\text{O}/\text{TiO}_2\) are comparable to samples from the Siqueiros fracture zone (Saal et al., 2002, among others). These last two characteristics have been interpreted as resulting from a prior melting event of the source (Perfit et al., 1996; Danyushevsky et al., 2000; Cartigny et al., 2008), and their \(\delta D\) would suggest that the hydrogen left in the residue after partial melting is depleted in D. However, the apparent correlation is not significant if those two samples are not taken into account, as might be expected if the high \(\text{TiO}_2/\text{H}_2\text{O}\) ratios reflect a specific process like a prior melting event.

4.5. A reference zone for the study of the N-MORB source

Previous studies on the \(\delta D\) values of N-MORB have mainly focused on samples from the North Atlantic and Pacific oceans (Kyser and O’Neil, 1984; Poreda et al., 1986; Pineau and Javoy, 1994; Pineau et al., 2004; Hauri et al., 2006; Cartigny et al., 2008). These studies concluded that the uncontaminated N-MORB source had a \(\delta D\) of −80 ± 10‰ (even if the average value measured in those studies is closer to −70‰). Most of those studies also used an extraction technique (induction heating in Pt crucibles) which can cause biases of more than 10‰ (Clog et al., 2012). The recent study of Bindeman et al. (2012), which does not use crucibles however, found the \(\delta D\) of Macquarie Island basalts to be close to −75 ± 5‰. Although falling within the canonical mantle range, it must be noted that those samples are very enriched compared to N-MORB (\((\text{La}/\text{Sm})_N > 1.3\) for the most depleted one) and are therefore not representative of the depleted mantle.

N-MORB from the North Atlantic measured with the same protocol as in this study (Clog et al., 2012) have \(\delta D\) of ≈−60‰ and do not outline the existence of a distinct \(\delta D\) between the Pacific–Antarctic and the North Pacific or Atlantic mantles. Nonetheless, the dataset is still restricted and we are going to evaluate whether this part of the upper depleted mantle can plausibly have a distinct \(\delta D\).

4.5.1. Geodynamic model

There are two ways to consider mantle water degassing flux at ridges. The first is that we observe degassing of some primordial water from the upper mantle (as for Craig and Lupton, 1976). In this case the apparent contrast with the North Atlantic and North Pacific could be inherited from the processes of crust extraction. This proposition is however unlikely. First, the South Pacific, the North Atlantic and the North Pacific mantle domains have very similar e.g. Sr isotopes compositions, suggesting an overall similar history and homogeneity resulting from mantle convection (van Keken et al., 2002; Hamelin et al., 2011, among others). Second, water is recycled in the mantle at subduction zones, which is likely to erase any primitive signature. This is illustrated by the high \(\text{H}_2\text{O}/\text{Ce}\) ratios in the North Atlantic due to recent rapid subduction (Michael, 1995) or by the distribution of \(\delta D\) observed in the Manus basin glasses (Shaw et al., 2012). It is thus unlikely that...
the southern Pacific mantle present a strong, inherited, δD contrast compared to the rest of the upper mantle.

The more generally accepted model considers the hydrogen cycle as in equilibrium chemically and isotopically (steady state), with water recycled into the convecting mantle at subduction zones (Iti et al., 1983; Bebout, 1995; Williams and Hemley, 2001; Dixon et al., 2002). This is supported by the stable continental freeboard in the last half-billion years and analysis of old hydrated rocks (Galer, 1991; Lécuyer et al., 1998). Recent estimates range from 0.2 to 2 ocean masses contained in the mantle (between 0.3 and 2.8 × 10^24 g; Bolfan-Casanova et al., 2000, 2005; Javoy, 2005; Keppler, 2006; Hirschmann, 2006), with half in the transition zone and very little in the lower mantle (less than 5% of the total water, although this number is highly model dependent, being sensitive to the oxygen fugacity of the transition zone and lower mantle). The large uncertainties on the amount of water in the mantle reflect the different hypotheses considered. With the current ridge and hotspot water output (10^{14} g/yr), the residence time is between 3 and 28 Gyr, but fluxes were probably greater during the Hadean and Archean and the equilibrium may have been reached early in Earth’s history. In this model, changing the composition of the upper mantle is possible by changing how recycling occurs, i.e., how much water is devolatilized, which P–T path the subducting slab follows, or depending on the thickness and extent of serpentinitization, for the mantle domains of the South Pacific and North Atlantic.

It should be noted that we have few direct constraints on the inward flux of water in the mantle, and especially on its isotopic composition. The subducting slab must lose more than 80% of its water (Nadeau et al., 1993; Chaussidon and Jambon, 1994; Dixon et al., 2002) to the arc system. The water content of the hydrated oceanic crust is between 0.5 and 5% with a δD between −30 and −50‰ (Kawahata et al., 1987; Kusakabe et al., 1989; Agrinier et al., 1995; Shilobreeva et al., 2011), but the sampling is very sparse, especially with respect to depth, and the hydration of the lower oceanic lithosphere is hard to constrain (Rüpke et al., 2004). To reach isotopic equilibrium of the water cycle, the final average δD of slabs after dehydration should be equal to the average δD of the ridges flux (e.g., −60‰, as measured in this study), but studies have given possible ranges from −30 to −200‰ for effectively recycled hydrogen (Kingsley et al., 2002; Shaw et al., 2008, 2012).

4.5.2. Changing the δD of the slab

An increase in the δD of the recycled crust before dehydration can be caused by changing either the δD of the ocean or temperature of alteration. The first is at odds with studies on ophiolites (Lécuyer et al., 1998) while the second requires an increase of several hundreds of degrees (Suzuuki and Epstein, 1976) compared to the current altered crust (Kawahata et al., 1987; Kusakabe et al., 1989; Agrinier et al., 1995), for which there is no compelling argument.

4.5.3. Subduction processes

The H2O/Ce ratios on the two supersegments studied here (186 ± 30 and 173 ± 15) are similar to those measured in the rest of the Pacific ridge system (between 150 and 220; Michael, 1995; Le Roux et al., 2006). A smaller extent of dehydration during subduction is therefore not a possible explanation for the apparent North Pacific/South Pacific δD contrast. Nevertheless, the exact P–T path followed by the slab depends on the dipping angle of the subduction zone (Hager and O’Connell, 1978; Cahill and Isacks, 1992). This could be critical for the final δD of the slab, as destabilization of the water-bearing minerals will occur at different pressures and temperatures (Schmidt and Poli, 1998; Kawamoto, 2006; Smyth, 2006). Water solubility in nominally anhydrous minerals depends on the pressure, so even for the same amount of dehydration (Kohlstedt et al., 1996; Mierdel et al., 2007), the final δD could differ. Indeed, even at 900 °C, fractionation of hydrogen isotopes between minerals is significant (up to 10‰; Suzuuki and Epstein, 1976; Graham et al., 1984; Dobson et al., 1989; Vennemann and O’Neil, 1996). This type of scenario would also create differences for other fluid-mobile elements like Li and B, and could explain the small differences between the two supersegments (δD ~ −63‰ in the south and δD ~ −58‰ in the north). Yet this scenario can hardly lead to the 20‰ contrast between our results and those of Kyser and O’Neil (1984). If we model the slab dehydration as an open-system loss of water, the average fractionation of water would need to differ by 10‰ (starting from identical hydrated rocks and ending with identical H2O/Ce ratios). Experiments on fractionation factors between water and hydrated minerals indicate that it corresponds to a ~150 C change in the range 500–900 °C (Suzuuki and Epstein, 1976). This explanation is therefore not satisfactory with the current view of P–T paths and dehydration of recycled ocean crust. However, this is a more plausible scenario to explain the small differences in δD (and H2O/Ce ratios) observed in our sample suite.

4.5.4. Revising the δD of the upper depleted mantle

We have shown that previous measurements could suffer from an experimental bias (Clog et al., 2012), and have not been able to find a satisfactory scenario explaining why the south Pacific would be enriched in D compared to previous data and other locations while being otherwise a perfect example of the upper depleted mantle, unaffected by mantle plumes. Our view is therefore that slight variations in δD (and H2O/Ce) can be produced by dehydration and recycling of water, but that the large contrast with previous data reflects analytical artifacts.

This sample suite presents many advantages to characterize the isotopic composition of the depleted mantle. Previous researchers have shown that the source composition is typical of the depleted mantle with limited and gradual variations in compositions in the area. Most of the variations are due to igneous processes, and the variation in spreading rate and ridge structure strengthens the conclusion that contamination is not a major obstacle to the determination of hydrogen isotopic composition of the source of N-MORB. Finally, the large number of samples (40 in this area compared to less than 70 N-MORB measured in a variety of locations in the literature; Craig and Lupton, 1976; Satake and Matsuda, 1979; Kyser and O’Neil, 1984; Poreda et al., 1986; Chaussidon et al., 1991; Pineau and Javoy, 1994; Kingsley et al., 2002; Pineau et al., 2004; Cartigny et al., 2008) limits the possibility of sample bias when calculating averages.

On the basis of this study, we propose that the average δD of the upper depleted mantle is −60 ± 5‰ rather than −80‰. Although the same average value and a similar range were observed on 8 N-MORB from the Middle Atlantic Ridge (Fig. 10; Clog et al., 2012), further studies on other ridges are necessary to confirm this figure. Variations observed in isotopic composition and water content shows that the upper mantle is not homogeneous, but present both small scale heterogeneities which are averaged by melts pooling when the spreading rate is higher than 7 cm/yr, and zonations at a larger scale leading to different average values on the northern and southern supersegments, illustrating the distribution of heterogeneities in the convecting mantle.

5. Conclusions

Despite widespread Cl contamination, assimilation of seawater-derived fluids or interaction with hydrated rocks did not significantly affect concentrations or isotopic compositions of hydrogen for our suite of samples. An increase in Cl contamination with
mainly due to igneous processes. The water content in the source
line program. This is IPGP contribution number 3433.
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spreading rate was observed. All samples are N-MORB with no evidence of influence from hotspots. Samples were under-saturated with respect to H₂O, and variations in concentrations of water are mainly due to igneous processes. The water content in the source ranges from 150 to 250 ppm. The average δD are −63 and −58‰ and the water to cerium ratios of 180 ± 30 and 173 ± 15 for the southern and northern supersegments respectively. The contrast with previous studies (δD ≈ −70‰) is not due to a difference during the recycling of water. It is rather explained by a combination of a potential experimental bias and different interpretation on the influence of contamination. The δD of the upper dePLETED mantle is close to −60 ± 5‰, with variations in δD and H₂O/Ce at different length scales resulting from recycling and ridge processes.

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Appendix A. Supplementary material

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References


