



The H/C ratios of Earth's near-surface and deep reservoirs, and consequences for deep Earth volatile cycles

Marc M. Hirschmann^{a,*}, Rajdeep Dasgupta^b

^a Dept. of Geology and Geophysics, 108 Pillsbury Hall, University of Minnesota, Minneapolis, MN, 55455, United States

^b Department of Earth Science, Rice University, 6100 Main Street, Houston, TX 77005, United States

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ABSTRACT

The H/C mass ratio of the Earth's exosphere, which consists of the fluid envelopes plus the crust, is 1.95 ± 0.15 . In contrast, the H/C ratios of undegassed oceanic basalts are significantly lower, ranging from 1.2 down to 0.05. Reconstruction of source H/C ratios by accounting for H/C fractionation during partial melting and addition of carbon-enriched low-degree partial melts suggests that the source regions of MORB have H/C ratios in the range of 0.75 ± 0.25 and those of OIB have ratios in the interval 0.5 ± 0.3 . Combining these estimates with plausible limits on the relative proportions of the OIB and MORB sources indicates that the total H inventory of the mantle is equivalent to between 0.2 and 1.6 times the H in the exosphere, assuming that there are no significant hidden reservoirs unsampled by oceanic basalts. Combining the H contents and H/C ratios of the mantle and the exosphere suggests that the H/C ratio of the bulk silicate Earth, $(H/C)^{BSE}$, is 0.99 ± 0.42 , significantly greater than the H/C ratio of chondrites, which have H/C ratios no greater than 0.55. The superchondritic $(H/C)^{BSE}$ ratio likely results from preferential sequestration of C in the core, though it may also partly reflect a cometary origin for some portion of the BSE volatile inventory. The high $(H/C)^{BSE}$ ratio, combined with a D/H ratio similar to chondrites, argues strongly that the BSE volatile inventory is not chiefly derived from a late veneer. The large difference in H/C ratio between the exosphere and the mantle could reflect early Earth processes such as preferential retention of C in a crystallizing magma ocean in reduced phases such as diamond, or selective loss of a massive CO₂-rich atmosphere. Alternatively, it may have arisen by enhanced subduction of carbon relative to hydrogen. If the latter is the case, carbon in the mantle is likely dominantly recycled.

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1. Introduction

Deep cycles of hydrogen (H) and carbon (C) are of fundamental importance to the long term evolution of terrestrial planets, as they have a principal influence on tectonics, climate, and habitability (McGovern and Schubert, 1989; Franck and Bounama, 2001; Hirschmann, 2006; Sleep and Zahnle, 2001; Hayes and Waldbauer, 2006). Key constraints on these cycles derive from the proportion of volatiles residing in near-surface reservoirs as compared to that portion stored in the deep interior. The relative distribution of volatiles between the surface and the deep interior reflect both the vigor of volatile exchange through time and the partitioning of different volatiles between these reservoirs and thus may contain clues to the processes that resulted in the observed distribution.

The present-day inventories of H and C on Earth's near-surface and deep reservoirs results from processes dating from the earliest Earth combined with later redistributing processes. The former include

delivery from and losses to space as well as degassing associated with magma ocean formation and early crust-forming processes. The latter include both continued magmatic degassing as well as ingassing associated with subduction or similar recycling processes (Sleep and Zahnle, 2001; Rüpke et al., 2004). Some H and C were presumably sequestered in the core early in Earth history, and this likely influenced the H/C ratio of the bulk silicate Earth, though fluxes of these volatiles from the core back into the mantle through geologic time probably are not significant, although not constrained. Thus, the H and C in the mantle are a combination of "primitive" and "recycled" inventories, where the former are those portions that have been in the mantle since 4.5 Ga and the latter have been returned to the mantle from near-surface reservoirs.

Naturally, mass fluxes between Earth's principal reservoirs during core formation, magmatism and subduction affect both H and C, but they may not do so equally. For example H and C may be fractionated during magmatism, as they have different mineral/melt partition coefficients (Saal et al., 2002; Hauri et al., 2006) and extensive C extraction may occur in deep domains in which H removal is less important (Dasgupta and Hirschmann, 2006). Similarly, there are significant differences in the petrologic behavior of H and C during subduction (Yaxley and Green,

* Corresponding author.

E-mail address: Marc.M.Hirschmann-1@umn.edu (M.M. Hirschmann).

1994; Kerrick and Connolly 1998; Molina and Poli, 2000; Kerrick and Connolly, 2001a,b; Connolly, 2005; Thomsen and Schmidt, 2008; Poli et al., 2009). Thus, one may expect that the H/C ratios of different reservoirs may have become fractionated and that these fractionations may provide some clues about the character and large-scale volatile fluxes through Earth history. The H/C ratios of Earth's near-surface and interior reservoirs are therefore of significant interest to studies of deep Earth volatiles cycles, but have received little attention. Here we examine these ratios and consider the processes that may be responsible for large scale H/C fractionations on Earth.

2. Inventories of H and C in the exosphere and in the mantle

The present-day mass of hydrogen in near-surface reservoirs (the crust, oceans, and atmosphere, which hereafter we refer to as the “exosphere”) is 1.8×10^{23} g of H (1.6×10^{24} g of H_2O) (Lecuyer et al., 1998). Carbon in the exosphere is stored chiefly in continental sediments and in the sedimentary and basaltic portions of oceanic crust (Javoy et al., 1982). Estimates for the present-day mass of carbon in the exosphere are somewhat variable. For example, those of Holser et al., (1988), Sleep and Zahnle (2001), and Hayes and Waldbauer (2006) are, respectively, 9.17, 8.5, and 10.2×10^{22} g. Other estimates, summarized by Hayes and Waldbauer (2006) are lower, but these commonly omit key reservoirs, such as carbonate in altered oceanic crust. We therefore take the exosphere carbon reservoir to be the average of these three estimates, or $9.3 \pm 0.9 \times 10^{22}$ g. Combining these estimates gives an H/C mass ratio for the exosphere, $(H/C)^{Exosphere}$, of 1.95 ± 0.15 .

The mass of Earth's H that is stored in the mantle is a matter of considerable interest and debate. The high propensity of some mantle silicates and particularly those in the transition zone to sequester hydrogen as OH (Kohlstedt et al., 1996; Bolfan-Casanova, 2005) means that the mantle could potential store many times the mass of H than is found in the oceans (Smyth, 1987; Williams and Hemley, 2001). Models of Earth's accretion that invoke addition of a volatile-rich late veneer similar to carbonaceous chondrites allow for a bulk Earth mass of H up to 4 times that in the oceans (Ringwood, 1975; Ahrens, 1989). This corresponds to up to 3 times that in the exosphere, i.e., 150 ppm H (1350 ppm H_2O) in the mantle, but observations from oceanic basalts do not support such large total masses of mantle H_2O .

Analyses of mid-ocean ridge basalts (MORB) indicate that the depleted source region, which likely comprises much of the upper mantle has 6–15 ppm H (or 50–150 ppm H_2O : Saal et al., 2002; Simons et al., 2002; Salters and Stracke, 2004; Workman and Hart, 2005) and that the enriched MORB and oceanic island basalt (OIB) sources have 40–100 ppm H (or 350–900 ppm H_2O : Sobolev and Chaussidon, 1996; Wallace, 1998; Dixon et al., 2002, 2008; Nichols et al., 2002; Simons et al., 2002; Aubaud et al., 2005). If the average mantle is an amalgam of sources sampled by MORB and OIB, then the total mass of H sequestered in the mantle is between 0.12 to 2.2 of the mass in the exosphere, or between 2.2×10^{22} and 4×10^{23} g of hydrogen. The former corresponds to a mantle made entirely of the driest MORB source, and the latter, to a mantle with the composition of the most hydrous OIB source. As neither of these extremes is realistic, the likely total H_2O content of the mantle is certainly within more narrow bounds. We return to this topic in Section 3.2.1 below.

It is possible that the total mass of H in the mantle exceeds 2 exosphere masses if there are significant volumes of H-rich mantle (with concentrations of $H_2O > 900$ ppm or $H > 100$ ppm) that are not sampled by modern oceanic basalts. This may be the case if there are significant hidden H-rich reservoirs, either in the transition zone (Smyth, 1987; Bercovici and Karato, 2003) or near the core mantle boundary (Panero et al., 2003). We note, however, that the transition zone water filter of Bercovici and Karato (2003), which requires that the transition zone is highly enriched in H, also posits that this material is sampled by modern oceanic island volcanism and therefore is not “hidden”.

The proportion of Earth's C that is stored in the mantle is less certain than that of H. This is because the sparing solubility of CO_2 in basalt at low pressure inhibits quantitative estimates of CO_2 concentrations in undegassed mantle-derived magmas. Estimates of mean mantle C concentrations range from 20 ppm up to 300 ppm (Javoy and Pineau, 1991; Trull et al., 1993; Zhang and Zindler, 1993; Marty and Tolstikhin, 1998; Sleep and Zahnle, 2001; Saal et al., 2002), which corresponds to between 0.9 to 14 times the exosphere C reservoir.

Owing to large uncertainties in the total H and C reservoirs in the mantle, H/C ratios estimated by permuting individual estimates of mantle H and C are not meaningful. For example, even excluding the extreme high estimate for carbon from Javoy and Pineau (1991), combining the ranges of individual H and C estimates produces H/C ratios varying by almost two orders of magnitude, from 0.1 to 4.4. A more fruitful approach is to examine the H/C ratios of undegassed basalts that might constrain the compositions of mantle source regions.

As mentioned above, erupted basalts generally undergo preferential degassing of CO_2 (Dixon and Stolper, 1995), thereby compromising analyzed C concentrations. These problems may be particularly significant for OIB, which may saturate in a CO_2 -rich gas at considerable depth owing to high initial carbon contents and which typically erupt subaerially or at shallow H_2O depths (Moreira and Sarda, 2000). However, valid H/C ratios of basalts potentially may be obtained if the basalts come from submarine eruptions from depths sufficient to avoid degassing (Dixon et al., 1997; Saal et al., 2002), if the analyses are performed on melt inclusions that are trapped at depth and sampled from rapidly quenched scoria (Bureau et al., 1998) or if strenuous efforts are made to reconstruct undegassed compositions from analysis of quenched glasses and vesicles with the aid of isotopic and rare gas

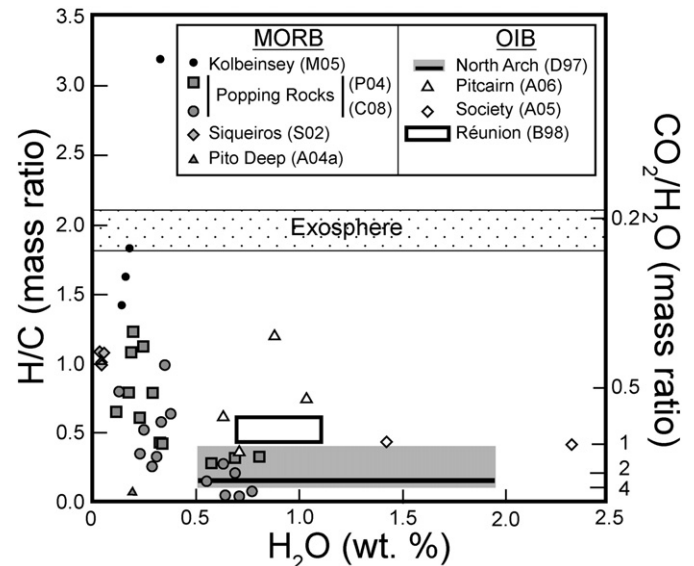


Fig. 1. H/C mass ratios versus H_2O contents of undegassed oceanic basalts. Data for MORB (filled symbols) include the 5 least degassed basalt from the Siqueiros Deep, East Pacific Rise (grey diamonds, S02: Saal et al., 2002), the North Atlantic popping rocks at 14° and $34^\circ N$ (grey squares, P04: Pineau et al., 2004; grey circles, C08: Cartigny et al., 2008), the Pito Deep, Easter Microplate (triangle, A04a: Aubaud et al., 2004a), and the Kolbeinsey Ridge (black circles, M05: Macpherson et al., 2005). The Pito Deep samples and the Kolbeinsey Rise samples are believed to be over-corrected and undercorrected for CO_2 -degassing, respectively (see text), and consequently their H/C mass ratios are believed to be, respectively, too low and too high. Data for OIBs (open symbols and rectangles) include data from the North Arch of Hawaii (grey shaded rectangle shows ranges of H/C and H_2O within uncertainties and heavy line shows best estimate of H/C for least degassed nephelinites, D97: Dixon et al., 1997), Réunion Island (rectangle shows the range of possible H/C and H_2O contents based on the data and estimates of Bureau et al., 1998: B98), the Society Islands (diamonds, A05: Aubaud et al., 2005), and Pitcairn Island (triangles, A06: Aubaud et al., 2006). Note that (except for the Kobleinsey samples), the basalts have significantly lower H/C ratios than the exosphere, for which $H/C = 1.95 \pm 0.15$ (stippled band). Also shown on the right axis are ratios calculated as CO_2/H_2O .

tracers (Pineau et al., 2004; Aubaud et al., 2004a, 2005, 2006; Macpherson et al., 2005; Cartigny et al., 2008). H/C ratios obtained in this way for MORBs and OIBs show considerable variations, ranging from 0.05 to 1.25 (Fig. 1). Importantly, these H/C ratios in these basalts may not be direct reflections of the ratios in their source regions, as H and C may be fractionated from each other during partial melting.

Fractionation of H from C during basalt petrogenesis may occur because C is more incompatible than H during partial melting (Pineau et al., 2004; Dasgupta et al., 2007), the former being highly incompatible with partition coefficients perhaps similar to Nb (Saal et al., 2002; Hauri et al., 2006), which means $D_{\text{H}}^{\text{peridotite/melt}} < 0.001$ (e.g., Salters et al., 2002) and the latter being modestly incompatible, with partition coefficients similar to a light rare earth element ($D_{\text{C}}^{\text{peridotite/melt}} = 0.005\text{--}0.009$; Michael, 1995; Aubaud et al., 2004b, 2008; Hauri et al., 2006; Tenner et al., 2009-this issue). Thus 1% and 2% partial melts will have H/C ratios that are up to 53–74% and 69–84% of the ratios in their sources, but higher percentages of partial melts will be more similar to their source; i.e., the H/C ratio of a 5% batch melt can be up to 85–93% of its source (Fig. 2). Much more variable ratios are possible for fractional melting. However, all but the smallest-degree fractional melts will have effectively no C and integrated fractional melts will be quite similar to batch partial melts.

These considerations can be applied to the observed H/C ratios of undegassed OIB displayed in Fig. 1. The ratios range from 0.16 to 1.2, but some of these basalts may have H/C ratios that are distinctly lower than the sources from which they are derived, owing to melting fractionation. For example, Dixon et al. (1997) estimated that the volatile-rich nephelinites from the North Arch of Hawaii were derived by $1.6 \pm 0.3\%$ melting, so the inferred H/C ratio of 0.16 for the undegassed basalts implies ratios of 0.19–0.25 in the source of these North Arch nephelinites. Similarly, the basalts from the Pitcairn, and Society localities have >5 wt.% K_2O (Aubaud et al., 2005, 2006), and consequently could be derived by $<1\%$ partial melting of their source. Thus, the Society lavas with reconstructed H/C of 0.4 (Aubaud et al., 2005) could derive from a source with H/C in the range of 0.55 to 0.77. Of course, this statement is model-dependent and the Society lavas have also been interpreted as a larger degree (5%) partial melt of a metasomatized source (Aubaud et al., 2005). The reconstructed Pitcairn basalts have highly variable H/C ratios, perhaps owing to partial degassing, different degrees of partial melting or source heterogeneity, and so it is difficult to infer a characteristic H/C ratio of their source, but the observed H/C ratios are broadly similar to those

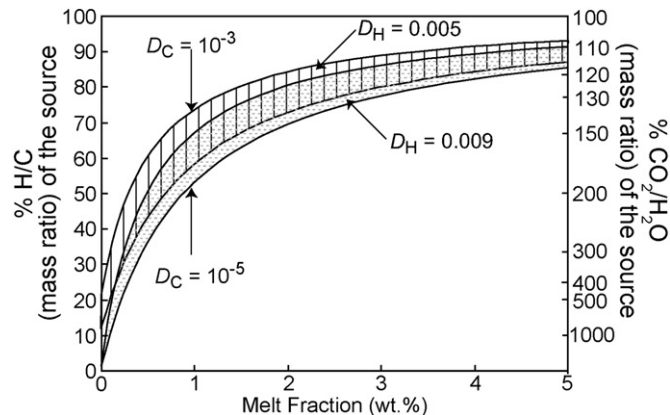


Fig. 2. Calculation of H/C fractionation as a function of degree of melting for a simple batch melting process, assuming that $D_{\text{H}}^{\text{peridotite/melt}} = 0.005$ or 0.009 (Michael, 1995; Aubaud et al., 2004b; Hauri et al., 2006; Tenner et al., 2009-this issue) and that $D_{\text{H}}^{\text{peridotite/melt}} = 10^{-3}$ or 10^{-5} . The stippled region is for $D_{\text{H}}^{\text{peridotite/melt}} = 0.009$ and the vertically lined region is for $D_{\text{H}}^{\text{peridotite/melt}} = 0.005$, with the upper and lower bounds of each region are marked by $D_{\text{H}}^{\text{peridotite/melt}} = 10^{-3}$ and $D_{\text{H}}^{\text{peridotite/melt}} = 10^{-5}$, respectively. The calculation shows that significant H/C fractionations are expected only when the degree of melting is small ($<2\%$). Also shown on the right axis are ratios calculated as $\text{CO}_2/\text{H}_2\text{O}$.

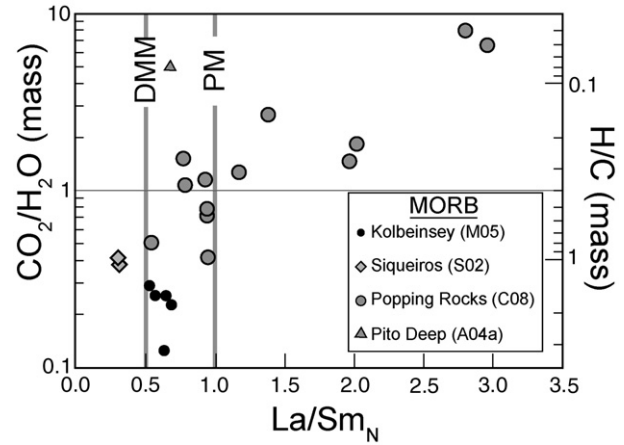


Fig. 3. $\text{CO}_2/\text{H}_2\text{O}$ ratios of undegassed MORB from North Atlantic popping rocks, the Siqueiros Fracture Zone, the Pito Deep, and the Kolbeinsey Ridge compared to primitive Earth (PUM)-normalized La/Sm ratios (PM from McDonough and Sun, 1995). $\text{CO}_2/\text{H}_2\text{O}$ and La/Sm_N sources and symbols are as in Fig. 1, except for La/Sm_N for the Pito Deep (Hekinian et al., 1996). Variations in $\text{CO}_2/\text{H}_2\text{O}$ and La/Sm_N are taken to be related to variable addition of a deep CO_2 -rich fluid (Dasgupta and Hirschmann, 2006; Cartigny et al., 2008; Dasgupta et al., 2009-this issue) and we take the $\text{CO}_2/\text{H}_2\text{O}$ ratio of the normal depleted MORB source to be 0.55 ± 0.2 , based on the intersection of the popping rock-Siqueiros trend with the La/Sm_N ratio of the depleted mantle (DMM; Workman and Hart, 2005). As in Fig. 1, the $\text{CO}_2/\text{H}_2\text{O}$ ratios of Kolbeinsey and Pito Deep samples are believed to be too low and too high, respectively, owing to undercorrection and overcorrection for degassing. Also shown on the right axis are mass ratios calculated as H/C.

from other OIB. Finally, the melt inclusions studied from Réunion have much less extreme compositions, typically containing <1 wt.% K_2O and have been inferred to be 5–10% partial melts (Bureau et al., 1998). Such high degree melts should have H/C ratios quite similar to their source; i.e. 0.45–0.6.

Accounting for the influence of melting fractionation on observed H/C ratios of the basalts, we infer that the source regions of OIB have H/C ratios in the interval between 0.2 and 0.8. The former is similar to the very low H/C ratio observed from North Arch, Hawaii (Dixon et al., 1997) when adjusted for the effects of partial melting, the latter is at the high end of H/C ratios observed for OIB (except for one Pitcairn lava). This interval $(\text{H}/\text{C})^{\text{OIB}} = 0.5 \pm 0.3$ is consistent with the recent estimate for the composition of the Hawaiian plume $\text{H}/\text{C} = 0.29$ by Dixon et al. (2008). More careful studies of OIB are required to further constrain possible H/C ratios of OIB source regions.

Observed and reconstructed undegassed H/C ratios of MORB vary considerably (Fig. 1). Data from the Mid-Atlantic ridge at 14° N and 34° N (Pineau et al., 2004; Cartigny et al., 2008) and from the Siqueiros Deep on the East Pacific Rise (Saal et al., 2002) form a steep trend of diminishing H/C with increasing H_2O . Our interpretation of this trend follows closely the analysis of Cartigny et al. (2008), who noted that $\text{CO}_2/\text{H}_2\text{O}$ ratios for these samples correlate with CO_2/Nb and La/Sm ratios and inferred that such variations are unlikely to derive from variable degrees of partial melting of a homogeneous source and rather derive from variable addition of a CO_2 -rich deep fluid. Cartigny et al. (2008) assumed that the fluid was a carbonatite, whereas Dasgupta et al. (2009-this issue) have argued that the trend is more consistent with addition of a carbonated silicate melt, but the key point is that both interpretations imply that the H/C composition of the MORB source is likely to be at the high end of the trend evident in Fig. 1.

To estimate the H/C ratio of the MORB source, we examine the trend of $\text{CO}_2/\text{H}_2\text{O}$ versus La/Sm_N first discussed by Cartigny et al. (2008). This trend (Fig. 3) intersects the La/Sm_N value of the depleted mantle (DMM) reservoir (La/Sm_N = 0.503; Workman and Hart, 2005) at a $\text{CO}_2/\text{H}_2\text{O}$ value in the interval of 0.55 ± 0.2 , which corresponds to an $(\text{H}/\text{C})^{\text{MORB}} = 0.75 \pm 0.25$. It intersects the primitive mantle

value of La/Sm_N (which is, by definition, unity) at a $\text{CO}_2/\text{H}_2\text{O}$ value of approximately unity, which corresponds to an H/C ratio of 0.4. Our analysis differs somewhat from that of Cartigny et al. (2008), who took the mean MORB $\text{CO}_2/\text{H}_2\text{O}$ ratio to be near unity, in other words, similar to that of the primitive mantle. The Cartigny et al. (2008) estimate may be applicable to the average upper mantle, as average MORB has $\text{La}/\text{Sm}_N = 0.881$ (Su, 2002). However, if the $\text{CO}_2/\text{H}_2\text{O}$ versus La/Sm_N trend observed by Cartigny et al. (2008) is derived from addition of a carbon-rich low degree partial melt to normal depleted MORB mantle (Cartigny et al., 2008; Dasgupta et al., 2009-this issue), and not from mixing of different mantle sources, it is not clear that intermediate compositions along the trend can be attributed to the composition of a mantle source. Our approach defines the likely composition of the depleted endmember of mantle compositions, and thereby places a lower limit on the $\text{CO}_2/\text{H}_2\text{O}$ ratio of the upper mantle.

Reconstructed degassed H/C ratios of MORB from the Kolbeinsey ridge (Macpherson et al., 2005) and from the Pito Deep on the Easter microplate (Aubaud et al., 2004a) have higher and lower H/C ratios, respectively, than the trend evident from the North Atlantic and Siqueiros localities (Fig. 1). Similarly, they plot to lower and higher values of $\text{CO}_2/\text{H}_2\text{O}$ at a given value of La/Sm_N (Fig. 3). Macpherson et al. (2005) suggested that the CO_2 concentrations that they inferred for the Kolbeinsey basalts may not account for deep degassing or alternatively, that the basalts may have been contaminated during crustal interactions. The opposite problem may apply to the Pito Deep samples, as the very high (1 wt.%) initial CO_2 concentrations may result from overcorrection for degassing. Alternatively, the MORB source region could be highly heterogeneous on a global scale, in which case much more work will be needed to constrain the H/C ratio of the mantle.

The inferred H/C ratios for the sources of oceanic island basalts, $(\text{H}/\text{C})^{\text{OIB}}$, of 0.5 ± 0.3 and MORB $(\text{H}/\text{C})^{\text{MORB}}$ of 0.75 ± 0.25 are not the same, but they overlap. We do not know whether the ratios in these different environments are distinguishable or if the differences in the intervals reflects simply the large uncertainties in H/C ratios from both geodynamic domains. The large ranges estimated for both the OIB and MORB sources reflects the scatter in determinations from individual localities combined with uncertainties in reconstructing source compositions from undegassed lavas and our confidence in these estimated ranges is tempered the limited number of localities studied to date. It is unclear if the variations reflect actual differences in mantle source regions, partial degassing during ascent, or are in part artifacts of correction procedures. Because the variations observed in single localities span much of the world-wide range, it seems likely that the latter two factors may be important. More data constraining the H_2O and CO_2 contents of undegassed OIB and MORB are clearly needed. Importantly, present data clearly shows that the MORB source and OIB sources have H/C significantly lower than the exosphere (1.95 ± 0.15).

3. Discussion

3.1. The C contents of mantle domains

Consideration of the ranges of likely H contents and H/C ratios of the mantle allows revised estimates for the CO_2 contents of different mantle domains. Assuming that the most depleted end member (DMM) of the mid-ocean ridge source region contains 110 ± 55 ppm H_2O (Salters and Stracke, 2004; Workman and Hart, 2005) and that the H/C ratio is 0.75 ± 0.25 , then the C concentration is 16 ± 9 ppm (60 ± 35 ppm CO_2). This is similar to estimates of Salters and Stracke (2004) ($\text{CO}_2 = 50 \pm 12$ ppm) and Workman and Hart ($\text{CO}_2 = 36 \pm 12$ ppm), but it is dramatically lower than inferences based chiefly on popping rocks which suggest close to 1000 ppm CO_2 in the sub-ridge mantle (Javoy and Pineau, 1991). If the enriched domains that are the sources of oceanic island basalts have 300–

900 ppm H_2O and H/C of 0.5 ± 0.3 , then they contain between 33 and 500 ppm C (120 and 1830 ppm CO_2).

3.2. H/C ratio of the bulk silicate Earth

3.2.1. Constraints on $(\text{H}/\text{C})^{\text{BSE}}$ and comparison to chondrites

The H/C ratio of the bulk silicate Earth, consisting of both the mantle and the exosphere, is imperfectly constrained owing chiefly to uncertainties in the H/C ratio and mean concentrations of volatiles of the mantle. However, if we assume that there are no appreciable hidden reservoirs of H or C in the mantle, then useful estimates can be made. To do this, we construct a Monte Carlo simulation for $(\text{H}/\text{C})^{\text{BSE}}$ that combines the exosphere with the mantle

$$\left(\text{H}/\text{C}\right)^{\text{BSE}} = \frac{M_{\text{H}}^{\text{Exosphere}} + M_{\text{H}}^{\text{Mantle}}}{M_{\text{C}}^{\text{Exosphere}} + M_{\text{C}}^{\text{Mantle}}} \quad (1)$$

where M_i^n is the mass of hydrogen or carbon in reservoir n , and the mantle consists of two different domains corresponding to the sources of OIB and the sources of MORB:

$$M_{\text{H}}^{\text{Mantle}} = xM_{\text{H}}^{\text{OIB}} + (1-x)M_{\text{H}}^{\text{MORB}} \quad (2a)$$

$$M_{\text{C}}^{\text{Mantle}} = xM_{\text{C}}^{\text{OIB}} + (1-x)M_{\text{C}}^{\text{MORB}} \quad (2b)$$

where x is the proportion of OIB-source in the mantle. The masses of C in each reservoir are calculated from the masses of H and the H/C ratios:

$$M_{\text{C}}^{\text{Exosphere}} = M_{\text{H}}^{\text{Exosphere}} / (\text{H}/\text{C})^{\text{Exosphere}} \quad (3a)$$

$$M_{\text{C}}^{\text{OIB}} = M_{\text{H}}^{\text{OIB}} / (\text{H}/\text{C})^{\text{OIB}} \quad (3b)$$

$$M_{\text{C}}^{\text{MORB}} = M_{\text{H}}^{\text{MORB}} / (\text{H}/\text{C})^{\text{MORB}} \quad (3c)$$

We take the relative volume of OIB source in the mantle to range between 10 to 70%, with the balance composed of MORB-source composition, and any given proportion of OIB-source within that interval is assumed to have equal probability. The minimum in this range corresponds to the minimum mass of the depleted mantle required to balance formation of the continental crust (Workman and Hart, 2005) and can also be justified based on long-standing notions equating the depleted mantle with the upper mantle (Allègre et al., 1983); the maximum corresponds to geochemical and geodynamical models that suggest that the OIB source region is a relatively limited reservoir, possibly associated with the D'' region (Hofmann, 1997 and references therein). The exosphere is taken to have 1 exosphere mass of H (1.8×10^{22} g) and $(\text{H}/\text{C})^{\text{Exosphere}}$ of 1.95 ± 0.15 , whilst the individual MORB and OIB reservoirs are assumed have 100 ± 50 and 600 ± 300 ppm H_2O , with H/C ratios ranging between 0.75 ± 0.25 and 0.5 ± 0.3 , respectively. These variations in concentrations and ratios are represented as normal (Gaussian) distributions, with the stated intervals corresponding to 2σ uncertainties.

The results of the Monte Carlo simulation are shown in Fig. 4. The resulting mass of H in the mantle ranges from 0.2 up to 1.6 exospheres, with a mean value of 0.65 and the mean mantle H/C ratio is 0.53 ± 0.28 (2σ), meaning that the more H-rich OIB dominates this ratio. When the proportion of H_2O -poor MORB-source is comparatively large, values of $(\text{H}/\text{C})^{\text{BSE}}$ cluster between 1 and 1.5 and when the proportion of H_2O -rich OIB-source is comparatively large they cluster between 0.5 and 1. The mean H/C ratio of all simulations is 0.99 ± 0.42 (2σ).

A vital clue to the origin and history of Earth's volatiles is a comparison between $(\text{H}/\text{C})^{\text{BSE}}$ and the H/C ratio of chondrites. Chondrites vary in their H/C ratios, depending on their type, but

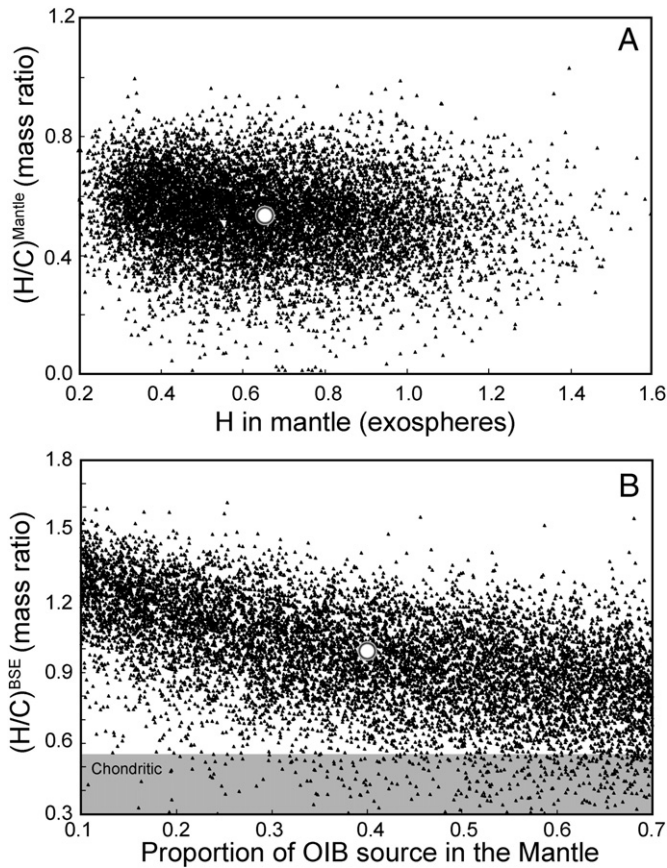


Fig. 4. Monte Carlo simulations of the H/C ratio of the silicate Earth. 10,000 simulations calculate the BSE ratio by assuming a range of H/C ratios of the exosphere (crust plus fluid envelopes) that is normally distributed about a mean value of 1.95 ± 0.15 (all uncertainties are 2σ). The mantle is assumed to consist of two reservoirs, the MORB-source and the OIB-source, with possible proportions ranging from 10 to 70% OIB-source and 90 to 30% and each simulation having an equal probability of a value within that range. The MORB-source has 100 ± 50 ppm H_2O and an H/C ratio of 0.75 ± 0.25 and the OIB source has 600 ± 300 ppm H_2O and an H/C ratio of 0.5 ± 0.3 . The simulation produces a normally distributed range of concentrations and ratios for each of these. (A) shows the spectrum of simulated mantle H contents, which ranges from 0.2 exospheres up to 1.6 exospheres and H/C ratios, which apart from statistical outliers, ranges from 0.2 to 0.8. (B) shows the spectrum of bulk silicate Earth (BSE) H/C ratios as a function of the proportion of OIB-source mantle. The range of H/C ratios in chondrites (Kerridge, 1985) is shaded in gray. 95% of the simulations produce $(\text{H}/\text{C})^{\text{BSE}}$ ratios greater than the maximum for CM chondrites (0.55) and 99.5% produce $(\text{H}/\text{C})^{\text{BSE}}$ ratios greater than typical for CI chondrites (0.3).

they are confined to the interval between 0 in enstatite chondrites (Kung and Clayton, 1978; Wasson and Kalleyman, 1988; Javoy, 1998) up to 0.55 in CM carbonaceous chondrites (Kerridge, 1985) (Fig. 5). CI chondrites, which are commonly used as models for Earth's bulk composition (e.g., McDonough and Sun, 1995) have H/C ratios no greater than 0.3 (Kerridge, 1985). Importantly, 96% of all the simulations produce $(\text{H}/\text{C})^{\text{BSE}}$ ratios greater than 0.55 and 99.5% produce ratios greater than 0.30. Admittedly, these statistics are partly a consequence of choices for the H_2O concentrations and H/C ratios of MORB and OIB source regions, for which true uncertainties could be larger than estimated and which await further constraints on the H and C concentrations of the mantle. However, unless the estimates employed are grossly in error, it is highly likely that the H/C ratio of the BSE is superchondritic. Near-chondritic ratios are likely only if the mantle is composed chiefly of the OIB source region and if the average H/C ratio of the OIB source is on the low side of plausible values.

Given that Earth's volatiles may have been delivered chiefly by planetesimals with composition similar to carbonaceous chondrites (e.g., Morbidelli et al., 2000), it is interesting that the bulk silicate Earth

H/C ratio, $(\text{H}/\text{C})^{\text{BSE}}$, likely exceeds that of even the most H/C enriched classes of carbonaceous chondrites (Figs. 3 and 4). The superchondritic $(\text{H}/\text{C})^{\text{BSE}}$ ratio may have arisen from one or a combination of processes related either to the cosmochemical supply of volatiles, selective loss of the atmosphere to space or to core formation.

3.2.2. Extraterrestrial origin of high $(\text{H}/\text{C})^{\text{BSE}}$?

One possible origin for the high $(\text{H}/\text{C})^{\text{BSE}}$ ratio is input from either comets or from nebular gas. For example, the ejecta from the Deep Impact experiment on 9P/Tempel 1 had a mean H/C mass ratio of 2.06 (Lisse et al., 2006). Many earlier measurements on cometary compositions indicated much lower H/C ratios that were similar to those of carbonaceous chondrites (e.g., 0.20 ± 0.06 for dust from Comet Halley, Jessberger et al., 1988), however these were chiefly measurements of cometary dust and may not have accounted properly for H_2O -rich gases and ices. But cometary hydrogen has a D/H ratio of about $3.0 \pm 0.1 \times 10^{-4}$ (Horner et al., 2006), almost exactly twice that of ratios on Earth ($1.49 \pm 0.03 \times 10^{-4}$, Lecuyer et al., 1998) and so significant cometary sources of volatiles would have to be balanced by coequal amounts of low D/H nebular gas ($0.25 \pm 0.05 \times 10^{-4}$; Javoy, 2005; Marty and Yokochi, 2006). Indeed, a small solar component in the mantle is required by Ne isotopes (Honda et al., 1991). But, if Earth's D/H ratio is a result of mixing between a solar nebular component and a cometary component, then the fact that its D/H ratio is encompassed by those of chondritic values has to be a coincidence. Moreover, when considered together, $^{15}\text{N}/^{14}\text{N}$ and D/H isotopic ratios rule out mixing between solar component and cometary component to generate the terrestrial nitrogen isotope ratio (Marty and Yokochi, 2006). The terrestrial nitrogen isotope ratio ($^{15}\text{N}/^{14}\text{N} = 3.68 \times 10^{-4}$; Marty and Dauphas, 2003), is more consistent with origin from sources similar to meteorites and micrometeorites ($^{15}\text{N}/^{14}\text{N} = 3.3\text{--}4.2 \times 10^{-3}$; Kerridge, 1985; Marty et al., 2005).

3.2.3. Origin of high $(\text{H}/\text{C})^{\text{BSE}}$ or high $(\text{H}/\text{C})^{\text{Exosphere}}$ by removal of a thick CO_2 atmosphere?

Another possibility is that the high $(\text{H}/\text{C})^{\text{BSE}}$ ratio could be a product of ablative processes. Hydrodynamic escape (Zahnle and Kasting, 1986) would not produce high $(\text{H}/\text{C})^{\text{BSE}}$, as it would cause preferential loss of H relative to C. However under certain circumstances, loss of an early CO_2 -

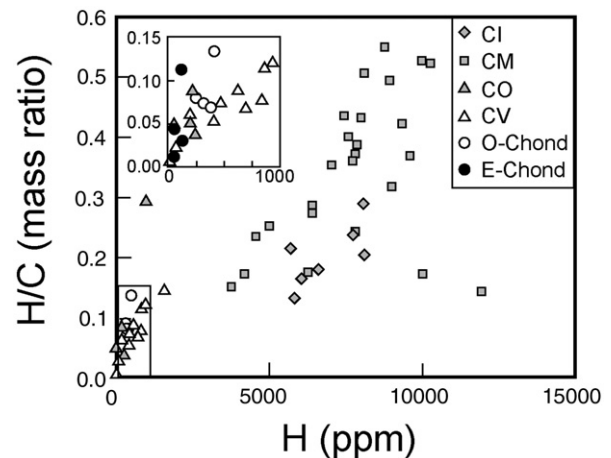


Fig. 5. Variations in H/C mass ratios in different classes of carbonaceous chondrites (CI, CM, CO, and CV; Kerridge, 1985) as a function of total H content. Also shown are data for ordinary chondrites (O-chond; Robert and Merlivat, 1979; McNaughton et al., 1981; Grady et al., 1989) and the ranges of H/C ratios for enstatite chondrites (E-chond) summarized by Javoy (1998), based on the H and C analyses of Kung and Clayton (1978) and Wasson and Kalleyman (1988) respectively. Enstatite chondrites are shown only in the inset, which shows the compositions of H_2O -poor samples more clearly. The highest H/C ratios are 0.55, from CM chondrites, define the maximum possible H/C ratio from chondritic sources. CI chondrites, which may otherwise be a better best match to the volatile-rich component on Earth (Javoy, 2005) have H/C ratios no greater than 0.3.

rich atmosphere owing to impacts (Melosh and Vickery, 1989; Genda and Abe, 2005) could increase the H/C ratio of the Earth. Formation of a CO₂-rich atmosphere could occur either during degassing of a magma ocean (Elkins-Tanton, 2008) or soon thereafter, when near-surface conditions allow formation of a liquid water ocean, leaving an atmosphere consisting chiefly of CO₂ (Zahnle et al., 2007). Of these two, it is the second that has greatest potential to allow for significant loss of a low H/C vapor from Earth.

If H₂O is retained during crystallization of a magma ocean owing to greater solubility of H₂O than CO₂ in magma and/or sequestration in silicates in the transition zone and elsewhere (Abe, 1997), magma ocean degassing could conceivably result in a thick CO₂-rich atmosphere with low H/C ratio. Removal of this atmosphere by a giant impact or by many smaller impacts could then increase the H/C ratio of the Earth. However, it is usually considered that degassing of a magma ocean creates a thick steam atmosphere (e.g., Matsui and Abe, 1986; Zahnle et al., 1988) and models that explicitly consider retention of H₂O in minerals crystallizing from a magma ocean predict that the efficiency of H₂O degassing to be similar to that of CO₂ (Elkins-Tanton, 2008). Therefore, magma ocean degassing probably did not produce an early low H/C atmosphere.

Following magma ocean crystallization, a CO₂-rich, H₂O-poor atmosphere amounting to many bars of CO₂ pressure can form once surface conditions were sufficiently cool to allow precipitation of a liquid water ocean (e.g., Zahnle et al., 2007). Genda and Abe (2005) investigated the dynamics of atmospheric loss owing to the Moon-forming giant impact for a planet with a global ocean. They found that significant removal of the atmosphere can occur without significant loss of the H₂O from the ocean, and that the key variable for volatile loss is the atmosphere/ocean mass ratio. However, their simulations showed that the mass of atmosphere that can be removed is only a small fraction of the mass of ocean present. For example, for an ocean mass similar to that at present, the maximum C loss in their simulations was 4.4×10^{22} g. This is a modest loss compared to BSE inventories. Depending on the total H and C concentrations in the modern mantle, the total carbon loss required to account for the superchondritic value of (H/C)^{BSE} ranges between 1.8×10^{23} g (for a modern mantle with 0.2 exospheres of hydrogen and an H/C ratio of 0.5) up to 5.9×10^{23} g (2 exospheres of hydrogen in the mantle and an H/C ratio of 1.0). The influence of 4.4×10^{22} g of C loss to space on the H/C of the exosphere would also be small. For example, assuming that the exosphere was chondritic prior to the impact (H/C = 0.55) and had 1 modern exosphere of H (1.8×10^{23} g), loss of 4.4×10^{22} g of carbon to space would increase the H/C ratio to 0.64. Therefore, partial loss of a CO₂-rich atmosphere owing to a giant impact does not seem capable of accounting for the high values of (H/C)^{BSE} or (H/C)^{Exosphere} in the modern Earth.

3.2.4. Origin of high (H/C)^{BSE} by C sequestration in the core?

Alternatively, the high (H/C)^{BSE} ratio could result from preferential sequestration of C in the core (Kuramoto and Matsui, 1996; Kuramoto, 1997). In fact, only modest concentrations of C in the core are required to balance the superchondritic H/C ratio of the BSE such that the whole earth is chondritic. For the carbon mass deficits outlined in the previous Section (1.8 – 5.9×10^{23} g), the C concentration in the outer core must exceed the concentration of H by no more than 100–320 ppm by weight to create an Earth with H/C ≤ 0.55 (assuming that both H and C in the inner core are negligible). Indeed, as pointed out by Kuramoto and Matsui (1996), the very low C/³⁶Ar of the BSE may suggest that the concentration of C in the core is considerably greater than a few hundred ppm. The solubility of C in core-forming melts is temperature dependent, but can be as high as 6–10 wt.% for the magma ocean temperatures of 2200–2700 °C (Dasgupta and Walker, 2008; Nakajima et al., in press; Lord et al., 2009). However, the actual carbon content of the core depends on the partition coefficient of carbon between coexisting metallic and silicate melts in a magma ocean and on the initial carbon content of the bulk Earth at the time of core-mantle

differentiation. Experimental constraints on partitioning of carbon between metal and silicate are lacking. But for equilibration of core and mantle melts in a bulk Earth with 1000 ppm C, mass balance predicts a carbon content of 0.25 ± 0.15 wt.% for the core (McDonough, 2003; Dasgupta and Walker, 2008). Partitioning of hydrogen between metal and silicate is also a matter of debate (Kuramoto and Matsui, 1996; Okuchi, 1997), but a similar mass balance calculation predicts a concentration of H in the core not exceeding 0.02 wt.% (McDonough, 2003). Thus experimental and mass balance constraints are consistent with a core that has a subchondritic H/C ratio (<0.1) and that has sufficient carbon excess relative to hydrogen to account for the high (H/C)^{BSE} ratio.

3.2.5. A role for a late veneer?

It has been suggested that Earth's volatiles, or at least those of the bulk silicate Earth, were delivered as part of a late veneer that post-dated principal giant impacts and core formation (Owen and Bar-Nun, 1995; Dauphas and Marty, 2002; Hauri et al., 2007). This idea is motivated in part from the premise that Earth may have lost most of its volatiles to space following a giant impact (Abe, 1997; Genda and Abe, 2005) and that the inventory of volatiles in the mantle and exosphere would therefore have to be replenished by later additions (Hauri et al., 2007). In this case, the (H/C)^{BSE} ratio would not be the result of core formation or the compositions of volatiles added during Earth's principal accretion stage, but instead would reflect the composition of the late veneer. The late veneer is commonly considered to be essentially chondritic (e.g., O'Neill, 1991; Holzheid et al., 2000; Hauri et al., 2007), but if the BSE volatiles derive chiefly from a chondritic late veneer, it is difficult to account for the present-day superchondritic (H/C)^{BSE}. The superchondritic (H/C)^{BSE} ratio requires either a non-chondritic source of BSE volatiles or that the BSE reservoir was established prior to equilibration between the mantle and core-forming materials. A more plausible scenario is that the late veneer consisted chiefly of ordinary and enstatite chondrites rather than carbonaceous chondrites, and therefore made a negligible contribution to the BSE volatile inventory (Fig. 5). A late veneer derived principally from ordinary and enstatite chondrites is arguably more consistent with the Os isotopes of the BSE (Shirey and Walker, 1998).

Although the present-day inventory of volatiles in the BSE cannot have been derived dominantly from a chondritic late-veneer, one may consider an alternative hypothesis in which the volatiles added in the late veneer contained a significant contribution from high H/C sources such as comets (e.g., Owen and Bar-Nun, 1995; Javoy, 2005). Dynamical simulations suggest that a modest (~10%) cometary contribution to terrestrial volatiles may be likely (Morbidelli et al., 2000). However, it has been argued that the high noble gas abundances of comets limit their contribution to Earth's volatile concentration to less than 0.1% (Dauphas and Marty, 2002). And as mentioned above, a cometary component of the late veneer would have high D/H (Horner et al., 2006), so accounting for the terrestrial D/H ratio would require that the cometary H mix with approximately an equal mass of H from a complementary very low D/H volatile component. The only known source of such a low D/H component would be nebular gas, but such gas could only have been added to Earth very early, and therefore could only participate in this mass balance if it remained in the mantle through Earth's early cataclysms (Javoy, 2005). If some nebular H remained in the mantle through giant impact and magma ocean processes, then some of the other H supplied during early accretion from planetesimals should have also, thereby obviating models requiring massive additions of volatiles from a late veneer. But more to the point, such a combination cannot account for the combined D/H, ¹³C/¹²C, ¹⁵N/¹⁴N ratios of the BSE (Marty and Yokochi, 2006).

In sum, it is unlikely that Earth's volatiles are dominantly from the late veneer. The combination of superchondritic (H/C)^{BSE} and chondritic D/H, and chondritic ¹⁵N/¹⁴N is most easily explained if the bulk of volatiles on Earth are chiefly from a chondritic source added during Earth's early accretion and if the high (H/C)^{BSE} evolved owing

to internal processes such as core formation. It is probable that an appreciable portion of the BSE volatile inventory survived giant impacts and magma oceans, either because it remained sequestered in the mantle or because removal of the atmosphere was incomplete (Genda and Abe, 2005).

3.3. Mantle-exosphere fractionation of H/C

Whether $(H/C)^{BSE}$ has been increased by supply of H rich materials from space and/or by sequestration of C in the core, neither process can explain the high H/C ratio of the exosphere compared to that of the mantle. Rather, the high H/C ratio of the exosphere requires either that H has been outgassed from the mantle in preference to C or that C has been ingassed from the exosphere in preference to H. Here we discuss key ingassing and outgassing processes and evaluate the likelihood that they are responsible for the key fractionation. Processes of interest include: (a) preferential retention of C relative to H during outgassing of a magma ocean, (b) preferential extraction of H relative to C during partial melting of the mantle, and (c) preferential subduction of C relative to H.

3.3.1. Retention of C in a crystallizing magma ocean

As noted above, magma oceans have the potential to outgas tremendous quantities of volatiles from the mantle (Matsui and Abe, 1986; Elkins-Tanton, 2008). This is because magma oceans do not form stable surficial crusts, but rather crystallize from the bottom up (Abe, 1997; Solomatov, 2000; Elkins-Tanton et al., 2005) and because they convect vigorously, thereby allowing effectively all of the magma to degas at low pressure. Consequently, regions of mantle that undergo a magma ocean stage have the potential to degas most of their H and C, creating a thick atmosphere and leaving behind a strongly volatile-depleted mantle (Elkins-Tanton, 2008). Because CO_2 is less soluble in magma than H_2O (Dixon et al., 1995) and because H_2O has a greater propensity to partition into crystallizing silicates (Keppler et al., 2003; Aubaud et al., 2004b; Hauri et al., 2006; Shcheka et al., 2006), magma oceans may preferentially degas carbon relative to hydrogen. This case, considered briefly in the section above on the H/C ratio of the bulk silicate Earth, would create the opposite sense of H/C exosphere/mantle fractionation observed on the modern Earth. However, it is conceivable that a crystallizing magma ocean could retain carbon in preference to H if a carbon-rich phase precipitates during crystallization.

Assuming that a magma ocean was associated with core formation, meaning the silicate magma equilibrated with molten metal, conditions of crystallization should be reducing and therefore the carbon-rich phases that could potentially precipitate from a magma ocean are diamond, graphite, and perhaps a metal carbide, rather than carbonate. The concentration of C in a silicate magma required for saturation with diamond or graphite depends on temperature, pressure, magma composition, and most critically, oxygen fugacity. Temperature and pressure have opposite effects, such that at fixed oxygen fugacity relative to metal-oxide buffers, the saturation concentration is near constant along the peridotite solidus and increases with increasing temperature above the solidus (Hirschmann and Withers, 2008). The oxidation state is critical, as there is a direct relationship between dissolved carbonate and oxygen fugacity (Holloway et al., 1992; Holloway, 1998; Hirschmann and Withers, 2008). Along the peridotite solidus and for oxidation states that might be consistent with recent equilibration with metal, or an oxygen fugacity one order of magnitude more reduced than the iron-wüstite (IW) buffer (Wood and Halliday, 2005), the concentration of dissolved C required to saturate in graphite or diamond could be as low as 2 ppm (Hirschmann and Withers, 2008). Thus, retention of C in a crystallizing magma ocean is plausible.

At present, the shallowest portions of Earth's mantle are probably too oxidized to permit saturation with graphite (Luth, 1999; Frost and McCammon, 2008). However, this is not inconsistent with the hypothesis that diamond or graphite precipitated in the mantle during

magma ocean solidification as the mantle becomes more reduced with increasing depth (McCammon, 2005), leading to stabilization of reduced carbon at depths of 200–300 km (Luth, 1999; Rohrbach et al., 2007; Frost and McCammon, 2008). Thus, if the magma ocean crystallized under redox conditions similar to the modern mantle, diamond crystallization would not have been impeded through much of the mantle depth interval and the solid residual mantle may have retained significant carbon. There is also the possibility that magma ocean crystallized under fairly reducing conditions and that soon thereafter the mantle was oxidized to near its present state by segregation to the core of a small additional fraction of melt (Wood and Halliday, 2005).

3.3.2. Preferential degassing of H during basalt extraction

If the high H/C exosphere is not a product of early Earth degassing processes, then another possibility is preferential outgassing of H relative to C during partial melting of the mantle, either beneath oceanic ridges or in intraplate environments. If H_2O were more incompatible than CO_2 in the residua of partial melting, then magmatic processes could outgas H_2O in preference to CO_2 and create a high H/C external reservoir. However, as we discussed in some detail above, evidence from modern oceanic basalts as well as from experimental measurements of mineral/melt partitioning suggests the opposite case – CO_2 is less compatible than H_2O and modern mantle magmatism outgases CO_2 in preference to H_2O .

If the mantle were more reducing, such that graphite rather than carbonate were stable in the source regions of oceanic basalts, carbon would be substantially more compatible. For example, thermodynamic models of melting in the MORB source region in the presence of graphite (Holloway, 1998) produce relations between dissolved C (as CO_2) and melt fraction with an effective partition coefficient $D_{CO_2}^{peridotite/melt}$ similar to 0.02–0.04 (Fig. 6). Observations from modern MORB (Saal et al., 2002; Cartigny et al., 2008) argue strongly that this is not the case at present, but it is less certain whether it could have been true early in Earth history. It has been suggested that basalt source regions in the Archean were more reducing than at present (Kump et al., 2001). If this were the case, then the high H/C exosphere could have arisen by volcanic

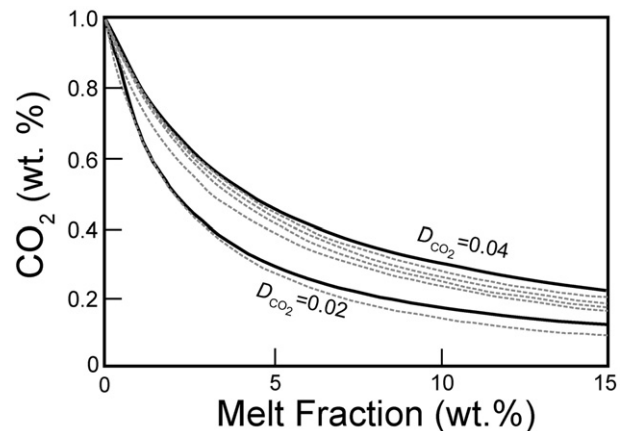


Fig. 6. Concentrations of CO_2 dissolved in partial melts formed by adiabatic melting of a graphite-bearing source beneath mid-ocean ridges, from thermodynamic calculations by Holloway (1998) (dashed lines). As detailed in Holloway (1998), the different curves correspond to calculations with different assumed initial ferric and ferrous iron contents in the source, different assumed temperatures, and different assumed mineral/melt partition coefficients for Fe^{3+} . These are compared to concentrations calculated by simple batch melting (solid lines) a source with 0.02 wt.% CO_2 and with a bulk melt/peridotite partition coefficient of 0.02 (lower curve) and a source with 0.04 wt.% CO_2 and with a bulk melt/peridotite partition coefficient of 0.04 (upper curve). These curves nearly bracket the thermodynamic calculations of Holloway (1998), demonstrating that the behavior of CO_2 during partial melting of a graphite-bearing mantle approximates that of an incompatible element with a partition coefficient similar to 0.02–0.04.

degassing in the Archean. However, studies of the redox state of mantle samples through geologic time argue against a pronounced secular evolution in mantle oxygen fugacity over the last 4 Ga (Canil and Fedortchouk, 2000; Li and Lee, 2004), which suggests that reduced Archean volcanic emissions are not the reason for the high H/C of the exosphere. In passing we note that it is not uncommon for thermodynamic models of redox behavior in modern MORB source regions to assume that graphite is present in the source region (Blundy et al., 1991; Holloway et al., 1992; Holloway, 1998). Such models are difficult to reconcile with evidence for highly incompatible behavior of C in mid-ocean ridge basalts.

3.3.3. Preferential subduction of carbon

The exosphere H/C ratio can also be increased relative to the mantle by preferential subduction of C into the mantle. The topic of recycling of volatiles to the mantle by subduction has received concerted attention in the Earth science community, and it is widely considered that both C and H may be returned to the mantle by this process (Kerrick and Connolly, 1998, 2001a,b; Dasgupta et al., 2004; Rüpke et al., 2004; Gorman et al., 2006), but perhaps with different efficiency. Consideration of metamorphic devolatilization reactions strongly suggests that devolatilization during subduction expels H in preference to C, producing residual slab with a very low H/C ratio (Yaxley and Green, 1994; Kerrick and Connolly, 1998, Molina and Poli, 2000; Kerrick and Connolly, 2001a,b; Connolly, 2005; Gorman et al., 2006). At least for the range of temperature–pressure paths likely for subduction in the modern Earth, melting reactions are not likely to remove the remaining carbonate by formation of either silicate (Yaxley and Green, 1994; Thomsen and Schmidt, 2008) or carbonatite (Yaxley and Brey, 2004; Dasgupta et al., 2004; Thomsen and Schmidt, 2008) magmas.

If mantle/exosphere fractionation of H/C ratios has been produced by subduction, then mantle and exosphere H/C ratios have been, respectively, decreasing and increasing through geological time. There is also the possibility that there have been secular changes in the style of volatile subduction in Earth history. For example, if slab partial melting were more common and more extensive in a hotter Archean mantle, subducting slabs may have been nearly completely dehydrated. However, it does not necessarily follow that all of the carbon would have been removed, as the solubility of CO₂ is very low in siliceous magmas formed from partial melting of slab components (Yaxley and Green, 1994; Thomsen and Schmidt, 2008). On the other hand, extraction of carbonatitic melts may occur for appropriately hot subduction temperatures (Dasgupta et al., 2004).

Also, if mantle/exosphere fractionation of H/C ratios has been produced by subduction, then this requires that the low H/C ratio of the mantle relative to the BSE has arisen by substantial additions of recycled carbon. In the simplest case if we assume (a) that volatiles are removed from the mantle in proportion to their mantle abundance and (b) that no H has been subducted, then we can estimate the minimum proportion of mantle carbon that has been recycled. This calculation indicates that subduction of carbon can explain the difference in H/C ratios between the mantle and the exosphere if 23 to 73% of carbon in the mantle has been subducted. The lower percentage is calculated from a total mantle H content of 1.6 exospheres and an (H/C)^{Mantle} of 0.8; the higher percentage is assuming 1.6 exospheres of mantle H and (H/C)^{Mantle} of 0.2 (Fig. 4A). Of course, if any H has been subducted, which is likely, correspondingly more C would also have to be. Therefore, we next consider the evolution of H/C ratios for the case where both H and C can be recycled.

There are many ways that one could simulate the history of H and C fluxes between the exosphere and the mantle that incorporate both degassing and subduction. Here we choose to develop a simple model that demonstrates the relationship between the total fluxes and the influence of preferential subduction of carbon. The models assume

that a large quantity of volatiles were degassed from the mantle at some early time in Earth history, without fractionating H from C, such that the exosphere mass of H, $M_{\text{H}}^{\text{exosphere}}$, became the same as at present. At this time, the exosphere mass of C, $M_{\text{C}}^{\text{exosphere}}$, is given by $M_{\text{H}}^{\text{exosphere}}/(H/C)^{\text{BSE}}$. Following this degassing event, the mantle contains a mass of H given by $M_{\text{H}}^{\text{mantle}}$, and a corresponding mass of C equal to $M_{\text{H}}^{\text{exosphere}}/(H/C)^{\text{BSE}}$. Following this initial event, H and C outgas through geologic time in a fixed number of time steps. The H/C ratios for volatiles outgassed are assumed to be that of the mantle at the time of outgassing (i.e., no fractionation of H and C occurs during partial melting). At each step, the mass of H that is ingassed via subduction, $m_{\text{H}}^{\text{ingas}}$, is fixed to equal the mass outgassed by magmatism, $m_{\text{H}}^{\text{outgas}}$, meaning that the masses of H in the exosphere and mantle do not change. Although small perturbations from this steady-state assumption are likely, it is broadly consistent with observations based on near-constant continental freeboard through geological time (Eriksson, 1999). A key feature of the model is that the carbon ingassed into the mantle is assumed to be greater than that of H by a factor β , such that $m_{\text{C}}^{\text{ingas}} = \beta m_{\text{H}}^{\text{ingas}}$. The time-integrated flux of H out of the mantle, $M_{\text{H}}^{\text{outgas}}$ is varied from zero up to 5 exosphere masses (up to 1×10^{24} g), and compositional evolution is calculated by finite time stepping. To do this, geological time (4.4 Ga) is divided into n steps. At each step, the flux of H out of the mantle is given by $m_{\text{H}}^{\text{outgas}} = M_{\text{H}}^{\text{outgas}}/n$. The flux of carbon out of the mantle is given by $m_{\text{C}}^{\text{outgas}}/(H/C)^{\text{Mantle}}$.

The results of these models are shown in Fig. 7. Fig. 7A shows the time evolution of the H/C ratio of the exosphere for several cases. Exosphere H/C ratios increase with increasing values of β and for a given value of β , they increase more when more total volatile subduction occurs (provided of course that $\beta > 1$). For very large masses of volatile subduction, H/C ratios of the reservoirs reach steady state. A key point is that the H/C ratio of the exosphere reaches values similar to the modern exosphere (1.95 ± 0.15) for relatively modest values of β , so long as there has been substantial volatile recycling through time. For example, if the total mass of subduction of H over the course of Earth history were equal to 0.5 exosphere masses and the subduction flux of carbon is just 2.5 times that of H, then the H/C ratio of the modern exosphere would exceed 2 (Fig. 7A).

In Fig. 7B we show two families of solutions that all produce an exosphere H/C ratio of 1.95. The first is for the case where the mantle contains 0.2 exospheres of H and the second the mantle contains 1.6 exospheres. If the total H subduction over geologic time is small, then the exosphere ratio can be produced so long as carbon subduction is much more efficient than H (i.e., β values near 10 for subduction of just 0.1 exosphere of H). With increasing total H subduction over geologic time, the H/C ratio of the exosphere reaches a steady state (Fig. 7A) and the value of β required to produce the desired exosphere composition diminishes small constant value between 1 and 2, with the exact value of this parameter depends on the assumed value of $(H/C)^{\text{BSE}}$. However, again the point is that modest enhancement of C subduction compared to H produces observed exosphere composition, so long as there has been extensive recycling of volatiles back into the mantle.

In Fig. 7C we show the relationship between the total amounts of carbon subducted to the present mantle inventory of carbon for the two families of solutions from Fig. 7B that produce the observed H/C ratio of the exosphere. These calculations show that the mantle is likely to be dominated by recycled carbon for most plausible mantle volatile inventories and flux histories. Only if the total mass of H in the mantle is large and the time integrated subduction flux of H is very modest can the time-integrated mass of subducted carbon be less than half of the present inventory of mantle carbon.

3.3.4. Primitive mantle-normalized concentration of exosphere volatiles compared to continental crust: the key role of C subduction

One enlightening strategy for gauging the relative vigor of carbon and hydrogen subduction is to consider the storage of these elements

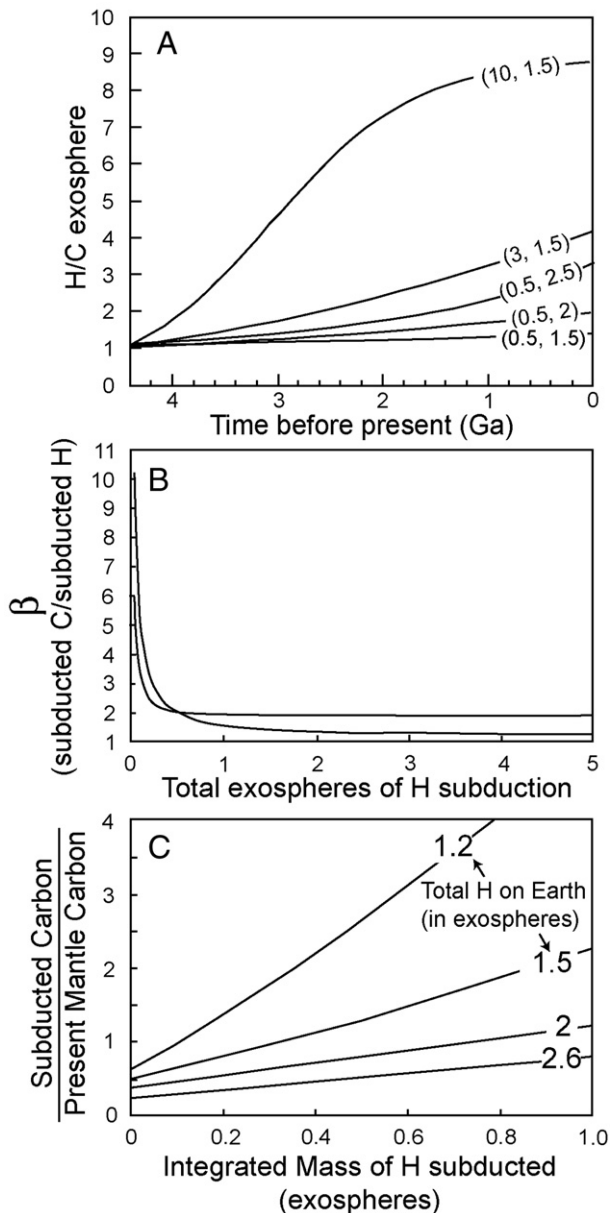


Fig. 7. Models simulating development of different H/C ratios between the mantle and the exosphere by subduction. All models have a total H and C inventory that consists of the sum of the present day exosphere H and C masses ($H/C = 1.95$) and a mantle with H mass varying from 0.2 to 1.6 exospheres and an $(H/C)^{\text{Mantle}}$ ratio equal to 0.53, the mean of simulations in Fig. 4A. At the outset of each calculation ($t=0$), the mantle and exosphere are assumed to have the same H/C ratio and the mass of H in the exosphere is assumed to be the same as at present. At each time step, equal masses of H are outgassed and ingassed from the mantle to the exosphere, but the H/C ratio of the outgassed volatiles is assumed to be the same as that of the mantle (no H/C fractionation during mantle melting) and the H/C ratio of the ingassed volatiles is assumed to have a fixed ratio given by the variable β . A shows the time evolution of models for several cases with varying integrated H subducted through all the time steps and values of β . These are indicated on each curve (integrated H, subducted, β). All calculations in A are for the case where the total H inventory in the BSE is equal to 2.6 exospheres (i.e., 1.6 exospheres of H in the mantle). Geologic time, beginning at 4.4 Ga, is divided into 100 time steps of 44 Ma, each. At each time step, the total H subducted is 1/100 of the total time-integrated H subduction. B and C are both for solutions in which the exosphere has an H/C ratio of 1.95 after a given amount of integrated H subduction. B shows the requisite value of β required to achieve the exosphere H/C of 1.95 for a given time-integrated H subduction flux for two cases of total H inventories in the BSE: one where the total mass of H in the BSE is equal to 2.6 exospheres (i.e., 1.6 exospheres of H in the mantle – solid curve) and the other where the total mass is equal to 1.2 exospheres (0.2 exospheres in the mantle – dashed curve). With smaller value of cumulative H subduction, larger values of β are required. C shows the relationship of total C subducted to total H subducted for total BSE H inventories ranging from 1.2, 1.5, 2, and 2.6 times the mass of H in the present exosphere.

in the exosphere in a manner analogous to storage of incompatible elements in the continental crust. This allows consideration of exosphere volatiles as long term differentiates from the bulk silicate Earth (or analogously, the primitive mantle in the sense of McDonough and Sun, 1995) owing to the combination of extraction of components from the mantle by melting and return to the mantle by subduction. The analogy between exosphere H and C and continental crust are justified because both the continental crust and exosphere volatiles (Ito et al. 1983; Sleep and Zahnle, 2001) have billion-year residence times in near-surface reservoirs.

To facilitate comparison between exosphere volatile concentrations and those of trace elements in continental crust, we calculate mean exosphere hydrogen and carbon concentrations by dividing their exosphere masses by the mass of the long-term near-surface reservoir, which includes the continental crust and the carbon and hydrogen volatile exosphere masses. Arguably, one could include the mass of the oceanic crust in this calculation, but we do not because its residence time in the near-surface environment is short (~100 Ma) and because doing so only diminishes the calculated concentrations by 20%. To compare these concentrations of H and C in the exosphere to those of the continental crust (Rudnick and Fountain, 1995), we normalize concentrations to the composition of the primitive mantle (McDonough and Sun, 1995). For the H and C concentrations in the primitive mantle, we take the mean estimate for the total H in the BSE (1.65 exospheres) combined with the mean $(H/C)^{\text{BSE}}$ ratio (0.99 ± 0.42) estimated in Section 3.2.1 (Fig. 4). These concentrations, of course are based on several assumptions, and we therefore consider the uncertainty in the primitive mantle H and C masses to encompass the range of values found in the Monte Carlo simulations depicted in Fig. 5. As a consequence, primitive-mantle normalized H and C concentrations are taken to lie within intervals that range by factors of ~2.2 and 4.6, respectively. Finally, we compare the primitive mantle-normalized H and C exosphere concentrations to those of the continental crust by plotting them in a compatibility diagram that scales with the relative propensity of the elements to be extracted from the mantle by partial melting (e.g., Hofmann, 1997), with C assumed to have a compatibility similar to Nb (Saal et al., 2002; Hauri et al., 2006) and H assumed to have a compatibility intermediate between La and Ce (Michael, 1995; Aubaud et al., 2004a,b, 2008).

The combined continental crust/exosphere volatile compatibility plot (Fig. 8) shows that H exosphere concentration is anomalous compared to the concentrations expected solely based on their

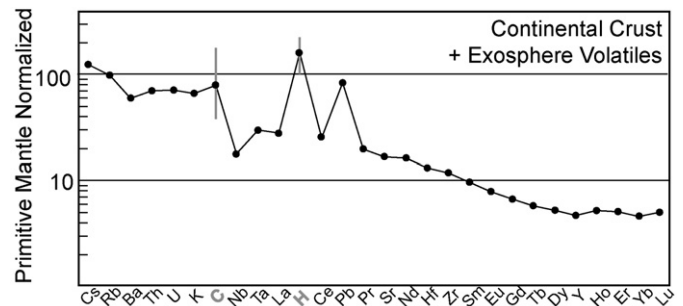


Fig. 8. Compatibility plot for exosphere plus continental crust inventory of C and H. The order and concentrations of trace elements is from Rudnick and Fountain (1995) and are normalized to primitive mantle concentrations from McDonough and Sun (1995). H is placed in between Nb and Ce, based on its relative compatibility during melting (Michael, 1995; Aubaud et al., 2004a,b, 2008; Hauri et al., 2006; Tenner et al., 2009-this issue) and C is placed between Nb and K, based on Saal et al. (2002). However, evidence from popping rocks suggests that Nb may be less compatible than Nb (Cartigny et al., 2008) and may belong further to the left on this diagram. For H and C, the mean concentrations of the continental crust plus exosphere is calculated from the mass of C and H in the exosphere divided by the mass of the continental crust plus exosphere. The mass of C and H in the primitive mantle (= bulk silicate Earth) is taken, with mean values from the average of simulations in Fig. 4 and uncertainties spanning the range of values found in the Monte Carlo simulations (0.2 to 1.6 exospheres of H in the mantle, mantle BSE ratios of 0.53 ± 0.3).

expected extraction efficiency from the mantle and that the C concentration is comparable to that of other highly incompatible elements, though the uncertainties for C are large. The anomalously high H concentration indicates that the H concentration in the exosphere is larger than one might expect based on its melting behavior, and the concentration of C demonstrates that the concentration of C in the exosphere may be similar to that expected based on its behavior during partial melting.

The strong positive H anomaly evident in Fig. 8 indicates that H is more abundant in the exosphere than one would predict based on the propensity of H to be removed from the mantle by partial melting. This excess H in the exosphere likely results from inefficient H subduction, which inhibits H ingassing, as has been surmised based on oceanic basalt geochemistry (Dixon et al., 2002) and the petrology of water subduction (Schmidt and Poli, 1998). Of course, the large H anomaly in Fig. 8 does not preclude H subduction, but only argues that the ratio of H that has been subducted compared to the flux of H extracted from the mantle by melting is smaller than the comparable ratio for elements that behave similarly during partial melting, such as La and Ce. In this respect, the behavior of H is similar to, but more extreme than, Pb, which resists subduction and therefore is heavily concentrated in the continents. We note that the excess of H in the exosphere could be a product of outgassing via modern processes such as melting at ridges, or alternatively, could be a remnant of extensive early outgassing that initially produced the oceans in the Hadean.

The placement of C on the compatibility plot (Fig. 8) is similar to that of neighboring elements U, K and Th. Given the large uncertainty in the C concentration, the actual location could either be anomalously high or anomalously low relative to the compatibility trend. A simple interpretation of this is that C removal from the mantle is similar to these highly incompatible elements and that also subduction of C is approximately as efficient as for these elements. But perhaps the key point is that the primitive mantle normalized abundance of C in the exosphere is similar to or lower than that of H, even though C has a greater propensity to be removed from the mantle during partial melting. This difference may well relate to enhanced subduction of C compared to H, which is consistent with petrologic analysis (Kerrick and Connolly, 1998; Molina and Poli, 2000; Kerrick and Connolly, 2001a,b; Dasgupta et al., 2004).

3.3.5. Secular variation in the exosphere carbon budget?

An important question regarding the long-term carbon cycle is the secular evolution of the budget of surface carbon. Models of the long-term terrestrial carbon cycle generally assume that the mass of surface carbon has increased through geologic time, as sediments have accumulated on the continents (e.g., Hayes and Waldbauer, 2006). The rationale behind such models seems quite persuasive, as only continents can protect reservoirs from recycling over long time scales and the available storage for carbonaceous sediments was at the outset limited by the presumably small continental area. A secular increase in surface carbon contrasts with the long-term H₂O cycle, as arguments from continental freeboard (Galer and Mezger, 1998; Eriksson, 1999) and early evidence for oceans (Wilde et al., 2001), indicate that the early surface inventory of H₂O was of comparable magnitude to that at present. Thus, if the surface inventory of carbon was initially small, then the H/C ratio of the exosphere was even larger than at present and has diminished with time. If true, this presents a significant conundrum in accounting for the origin and evolution of H/C ratios of Earth's principal reservoirs.

One explanation for H/C fractionation between the mantle and the exosphere is that it has arisen owing preferential subduction of carbon. This scenario requires that the H/C ratio of the exosphere has increased through time and therefore is directly in opposition to the idea that the exosphere carbon reservoir has grown substantially since early in Earth history. For example, the models in Fig. 7 assume that early in Earth history the oceans were the same size as at present and

that the exosphere had an H/C similar to the BSE, meaning that the early exosphere inventory of carbon was about twice that of the modern.

One possibility is that the massive outgassing that produced the early oceans also produced a corresponding inventory of surface carbon, but that this surface carbon, having little or no continental substrate to protect it from recycling, was rapidly returned to the mantle, perhaps through subduction. Earlier models (Javoy et al., 1982; Sleep and Zahnle, 2001) incorporate just such a massive early ingassing event. A range of other possible early Earth events might also be capable of accounting for the present-day H/C fractionation between the mantle and the exosphere. For example, a small early inventory of exosphere carbon could be a consequence of carbon sequestration during magma ocean crystallization, as discussed in Section 3.3.1. Alternatively, early loss of a CO₂-rich atmosphere, considered in Section 3.2.3, may have been more substantial than suggested by the models of Genda and Abe (2005). However, all of these scenarios imply that modern H/C fractionation between the mantle and the exosphere is a remnant of processes that occurred in the very early Earth. These scenarios all therefore imply that subsequent exchange between the mantle and exosphere has had only modest influence.

One further concern is the mechanism by which the exosphere carbon budget may have grown through time. If it has grown over the last 4 Ga (e.g., Sleep and Zahnle, 2001; Hayes and Waldbauer, 2006), it must have done so owing to mantle outgassing exceeding ingassing. This again suggests that the H/C ratio of the exosphere was higher than the modern value during the early Archaean and has diminished to the present ratio, and it also suggests that the total mass of subducted crust has had a high time-integrated H/C ratio over the last 4 Ga, as otherwise the exosphere H inventory should also have grown substantially. Perhaps during the Archaean, carbon ingassing was much less efficient than at present owing to higher mean subduction temperatures and consequent stripping of carbon by carbonatite melting (Dasgupta et al., 2004). Thus, modern H/C fractionation between the mantle and the exosphere could be the result of early Earth processes combined with complex and time-variable processes.

A key observation is that there is no evident secular evolution through geologic time in the carbon isotope ratios of carbonate rocks (Shields and Veizer, 2002). A number of models have been proposed to account for the carbon isotope record, including massive carbon recycling (Javoy et al., 1982), a balance between carbon subduction and carbon fluxes from deep reservoirs (Coltice et al., 2004), and a balance between oxidized and reduced subducted carbon (Hayes and Waldbauer, 2006). Ultimately, any secular evolution in the distribution of carbon between the mantle and the exosphere will also have to be reconciled with the carbon isotope record, but this lies beyond the scope of the present investigation.

3.3.6. A hidden reservoir could change everything

It also should be noted that the apparently low H/C ratio of the mantle as sampled by oceanic basalts could be unrepresentative of bulk mantle H/C ratios if there is a substantial hidden mantle reservoir with high H/C. To have a substantive effect on the mass balances presented in this paper, any hidden reservoir must be a significant volume of the mantle and/or have greatly enriched volatile inventory and it must have an H/C ratio significantly different from the mantle reservoirs sampled by oceanic basalts. For example, an H₂O-rich transition zone posited by the transition zone water filter hypothesis (Bercovici and Karato, 2003) could plausibly develop high H/C, though it would require a scenario in which melt-filtering sequestered hydrogen but not carbon. But as noted above, the transition zone water filter hypothesis posits that H₂O-enriched transition zone is sampled by oceanic island basalts, and the relatively low H/C source ratios evident from OIB data does not support the hypothesis that OIB come from a high H/C reservoir. Finally, the storage, fluxes, and petrologic behavior of volatiles in the lowermost mantle are not well

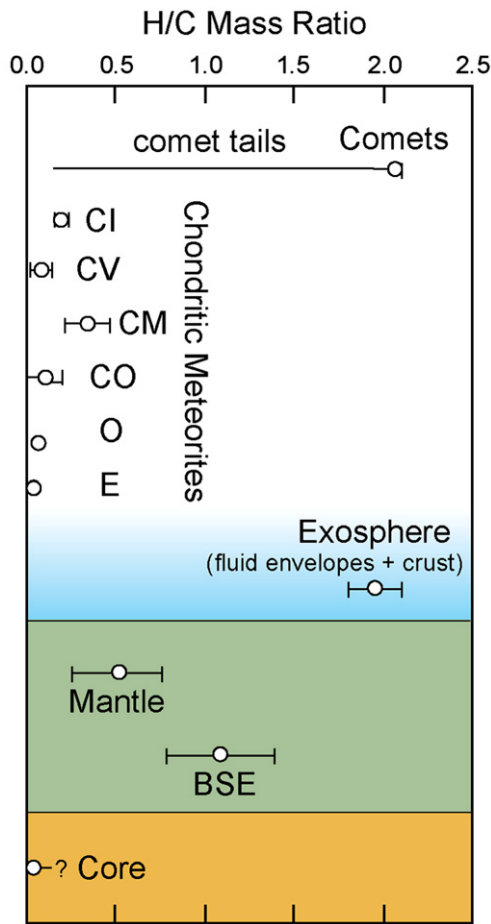


Fig. 9. Summary of the H/C ratios of different terrestrial and extraterrestrial reservoirs. The H/C ratios for meteorite classes are from Fig. 4. The sources for other measurements and estimates are described in the text.

understood and so the possibility of a volatile-enriched high H/C reservoir in D'' , somehow unsampled by OIB, perhaps cannot be excluded. For example, dense hydrous melts created in the lower mantle by dehydration of hydrous phases in subducted slabs could, over time, accumulate in the lowermost mantle if they are negatively buoyant in the lower mantle. If conditions in subducted slabs in the lower mantle are sufficiently reducing, carbon might not partition into such melts, but instead could be retained in diamond and so dense melts transporting volatiles to the core-mantle-boundary could have high H/C.

4. Concluding remarks

The H/C ratios of different terrestrial and extraterrestrial reservoirs based on the data and models considered in this paper are summarized in Fig. 9. The key points are: (a) The H/C ratio of the bulk silicate Earth is superchondritic, owing chiefly to the high H/C ratio of the exosphere. (b) the H/C ratio of the mantle is lower than that of the exosphere, which requires significant H/C fractionation during ingassing or outgassing at some point in Earth history.

The most plausible explanation for the superchondritic $(H/C)^{BSE}$ ratio is that the H/C ratio of the core is probably subchondritic, owing to preferential solution of C in metal during core formation. Extraterrestrial sources of high H/C materials, such as comets or nebular gas, may have contributed to the high H/C ratio of the bulk silicate Earth, but it is unlikely that these are the predominant source of Earth's volatiles, owing to the similarity between the D/H ratio and $^{15}N/^{14}N$ ratio of Earth and chondrites. A chondritic late veneer cannot be the predominant source of the bulk silicate Earth's volatiles, as it

cannot explain the high H/C of the BSE. A high H/C cometary late veneer could only contribute a modest portion of the BSE volatile budget, as it would have to be balanced by a large preexisting low D/H reservoir.

Differences in H/C ratios of the mantle and the exosphere could have arisen from several processes or from a combination of processes. These include retention of carbon during magma ocean crystallization owing to diamond precipitation, loss of an early CO_2 -rich atmosphere to space and preferential carbon subduction. The latter is an attractive mechanism because it accords with petrologic understanding of H_2O and carbon behavior during subduction. Further, the exosphere inventories of H and C are, respectively, larger than and similar to that expected simply based on their melting behavior, and this may be most easily explained by inefficient H subduction combined with very efficient C subduction. However, the secular changes in the C in the exosphere through geologic time may place important constraints on the key processes involved in C exchange between the surface and mantle, and these favor fractionation events that occurred early in Earth history.

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