



Volatile element abundance patterns and an early liquid water ocean on Earth

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Abstract

The abundances of the elements H, C, N, Ne, primordial Ar, Cl, Br, Kr, I and Xe, in the atmo-hydrosphere, continental crust and MORB-source mantle (termed the outer Earth reservoirs (OER)) are examined and compared with solar matter and an average of carbonaceous chondrites (CC). The aim is to assess the likelihood of various possible sources for these volatile elements now on Earth, and discuss and possibly quantify processes whereby volatiles were lost, in order to narrow down scenarios for the earliest terrestrial environment.

Al-normalized abundance patterns show a depletion relative to solar matter which varies from 2×10^{-11} for Ne to 4×10^{-3} for the halogens. The overall relative pattern is broadly similar to an average abundance pattern of CC, with two to three orders of magnitude depletion relative to this. For H, C, N and the halogens this similarity, against the background of the huge diversity compared to solar matter, makes CC-type material a much more likely source than a gravitationally captured solar atmosphere. A small admixture of solar matter ($Al_{\text{solar}}/Al_{\text{total}} \approx 10^{-7}$) acquired in accretion can account for the solar Ne isotope signatures in the deep mantle. The abundance pattern of C, N, Ne, primordial Ar, Br and Kr relative to such a “solar spiked” CC-type source shows depletions dependent of the masses of the molecules (C as CO, N as N₂, Br as Br₂), which can be modeled assuming a hydrodynamic escape mechanism with H₂ fluxes varying from 1 to 3×10^{13} molecules cm⁻² s⁻¹. Relative to this depletion pattern, H (as H₂O) and Cl (as HCl) are overabundant by about an order of magnitude. Delivery by comets over Earth history is a highly unlikely explanation for the H overabundance, as measured cometary D/H ratios are $\sim 2\times$, and C/H ratios $\sim 4\times$ higher than those of the OER. The overabundance of both H and Cl can be understood and quantitatively modeled if it is assumed that a liquid water ocean existed in which major portions (on average, between 50 and 70%) of H₂O and HCl resided during hydrodynamic escape, so that their volume proportion in the atmosphere (and therefore their loss) was reduced.

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1. Introduction

The question of whether a liquid water ocean existed on the early Earth is important for the origin and initial spread of life, as has been repeatedly stressed in recent years (e.g. Nisbet and Sleep, 2001). One in-

dication for the early existence of liquid water is provided by elevated $\delta^{18}\text{O}$ values up to +9%, reported in 4.1–4.3 Ga old detrital zircons from Jack Hills, Western Australia (Mojzsis et al., 2001; Wilde et al., 2001; Peck et al., 2001). In addition to the few >4 Ga zircons, the older population from Jack Hills contains many grains in the age range 3.9–4 Ga; these have Hf isotope ratios indicating that the crust in which they formed was derived from the mantle as early as 4.3–4.4 Ga

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(Amelin et al., 1999, 2000; Kramers, 2001). The high $\delta^{18}\text{O}$ values indicate that some form of rock–water interaction played a part in crust formation processes taking place around 4.3–4.4 Ga.

In view of the importance of the question, any possible evidence should be considered. The approach taken in this paper makes use of the abundances of the volatile elements H, C, N, Cl, Br, I, Ne, Ar, Kr and Xe, which are today strongly concentrated in the atmo-hydrosphere, sediments and their derivatives. It is assumed that an early atmo-hydrosphere containing these elements formed during the accretion and earliest history of the Earth by degassing from melts. The amounts of them that could have been inherited from such an atmo-hydrosphere are obtained by adding their abundances in the present atmo-hydrosphere, oceanic and continental crust and an estimated recycled component in the MORB-source mantle, which

is small in most cases. This ensemble is termed the outer Earth reservoirs (OER). A comparison of solar- and chondrite-normalized abundance patterns of the OER reveals an affinity with carbonaceous chondrites (CC), at least for H, C, N and the halogens. However, a striking feature of the CC-normalized pattern is an overabundance of H and Cl relative to C and N.

Possible sources of the terrestrial volatiles (CC, comets, a captured solar atmosphere or solar wind) are discussed, as well as the processes whereby they came into, and could have been lost from, the early atmosphere (volcanism; atmosphere loss by impact erosion or hydrodynamic escape). Notwithstanding many uncertainties, it is concluded that the H and Cl overabundance cannot be explained by any possible combination of sources, modes of delivery to the Earth, or processes within the Earth. Differential loss is considered as a possible cause for it, and the consequences

Table 1

concentrations of Al, H, C, N, Cl, Br and I (ppm) in average carbonaceous chondrite (CC) material, the Earth (Al) and the outer Earth reservoirs (OER, i.e. atmosphere, ocean, continental crust and MORB-source mantle)

Element	Average carbonaceous chondrites ^a	Earth (Al), OER (others) best estimate	Uncertainty limits (%)	OER/average carbonaceous chondrites
Al	13050	15070		1.1548
H	9375	35 ^b	±15	0.0033
C	16025	17 ^c	±30	0.0004
N	797.5	0.86 ^d	±10	0.0010
Cl	322.5	5.9 ^e	±10	0.018
Br	2.25	0.03 ^f	+100/–50	0.0151
I	0.33	0.0024 ^g	+100/–50	0.017

Abundances in the Earth and OER recalculated to mass of the whole Earth, including core.

^a Anders and Grevesse (1989), Wasson and Kallemeyn (1988).

^b Oceans, ice caps, freshwater, groundwater all together 1.364×10^{24} g H₂O, i.e. 1.515×10^{23} g H or 25.25 ppm H for whole Earth (mass 5.983×10^{27} g). Including continental crust with sedimentary and metasedimentary rocks (Lécuyer et al., 1998) brings total surface H up to 31 ppm. Mantle (see text) 1–7 ppm.

^c Total mass of carbon as carbonate in sediments and metasediments estimated at 3.5×10^{22} g (Ronov and Yaroshevskiy 1968; Wedepohl, 1995). Total organogenic carbon in crustal rocks is 1/4 of this (e.g. Schidlowski, 2001). Estimates similar to those of Lécuyer et al. (2000). Amounts of C presently in biosphere and atmo-hydrosphere are insignificant by comparison. Recycled mantle component probably as large as the crustal reservoir (see text).

^d The atmosphere has 3.85×10^{21} g N₂, 0.643 ppm of the Earth. Nitrate in sediments and metasediments make up 60 ppm of the continental crust (Wedepohl, 1995), i.e. 0.2 ppm of the whole Earth. Recycled mantle component is only about 3% of this (see text).

^e Oceans have 1.93% Cl, total 2.63×10^{22} g. The crust (mainly sediments and metasediments) add 9.6×10^{21} g. Together this is 6 ppm of the whole Earth.

^f Oceans have 67 ppm Br, 9.14×10^{19} g. Br in sediments and metasediments is dominated by originally C-adsorbed Br; a ratio of Br/C = 0.01 in organogenic carbon-rich sediments (Fuge, 1973a) gives 8.75×10^{19} g. Together this is 0.03 ppm of the whole Earth.

^g Oceans have 60 ppb I, 8.2×10^{16} g. Like Br, I in sediments is dominated by organic C-adsorption. I/C = 0.002 in organic-rich sediments (Fuge, 1973b; Muramatsu and Wedepohl, 1998). Bulk continental crust has 119 ppb I, 2.5×10^{18} g; oceanic crust 777 ppb, 6.1×10^{18} g; together 8.7×10^{18} g or 1.45 ppb of the Earth. Estimated amount of I in MORB-source mantle ca. 4 ppb (Wänke et al., 1984), or ca. 1 ppb of Earth.

of loss to space of atmospheric volatiles by hydrodynamic escape in the presence of a liquid water ocean are examined.

2. The volatile element abundance pattern of the outer Earth reservoirs

The atomic abundances of highly volatile elements in the OER are listed in Tables 1–3, and shown in Fig. 1a normalized to the terrestrial abundance of the highly refractory major element Al (I have chosen Al rather than the more commonly used Si, as Al is more refractory and is never suspected of partly

entering the core). In addition to the amounts in the atmo-hydrosphere and continental crust, the OER budgets include abundances in the MORB-source mantle, which may have a large component recycled from the surface reservoirs. The effective mass of the MORB-source mantle used to calculate the contribution to OER budgets is 1.4×10^{27} g, about 40% more than the “upper mantle” above the 670 km discontinuity (Allègre and Lewin, 1989; Allègre, 1997). This is in accord with the observation from seismic tomography that mantle convection includes the lower mantle to some extent (e.g. Van der Hilst and Kárason, 1999). The primitive, or undegassed, mantle reservoir and the core are not included in the budget

Table 2

Al-normalized atomic abundances of strongly volatile elements in average carbonaceous chondrites, solar matter, mixtures of these and the Earth surface reservoirs

Element	Average carbonaceous chondrites ^a	Solar matter ^b	Mix 1 average CC + 10^{-7} solar matter	Mix 1 average CC + 10^{-6} solar matter	OER reservoirs ^c
H	19.2	4.29×10^6	19.6	23.5	0.062
C	2.76	171	2.76	2.76	0.0025
N	0.118	34.3	0.118	0.118	0.00011
Cl	0.019	0.071	0.019	0.019	0.0003
Br	5.82×10^{-5}	1.4×10^{-4}	5.82×10^{-5}	5.82×10^{-5}	6.7×10^{-7}
I	5.35×10^{-6}	1.3×10^{-5}	5.35×10^{-6}	5.35×10^{-6}	3.4×10^{-8}
Ne	3.03×10^{-7}	50	5.3×10^{-6}	5.03×10^{-5}	1.28×10^{-9}
Ar	7.5×10^{-7}	1.43	8.9×10^{-7}	2.18×10^{-6}	1.99×10^{-9}
Kr	1.80×10^{-8}	5.3×10^{-04}	1.81×10^{-8}	1.85×10^{-8}	6.11×10^{-11}
Xe	2.52×10^{-8}	7.1×10^{-05}	2.52×10^{-8}	2.53×10^{-8}	4.57×10^{-12}

^a Noble gas data from Anders and Grevesse (1989), Ozima et al. (1998; “Q gases”).

^b Anders and Grevesse (1989).

^c Noble gas data: Ozima and Podosek (1983).

Table 3

Ratios of Al-normalized atomic abundances of strongly volatile elements

Element	Average CC/solar	OER/solar	OER/average CC	OER/(1 average CC + 10^{-7} solar)	OER/(1 average CC + 10^{-6} solar)
H	4.49×10^{-6}	1.45×10^{-8}	3.2×10^{-3}	3.2×10^{-3}	2.6×10^{-3}
C	0.0161	1.5×10^{-5}	9.2×10^{-4}	9.2×10^{-4}	9.2×10^{-4}
N	3.43×10^{-3}	3.2×10^{-6}	9.3×10^{-4}	9.3×10^{-4}	9.3×10^{-4}
Cl	0.263	4.2×10^{-3}	0.016	0.016	0.016
Br	0.408	4.7×10^{-3}	0.012	0.012	0.012
I	0.416	2.6×10^{-3}	0.006	0.006	0.006
Ne	6.06×10^{-9}	2.56×10^{-11}	4.22×10^{-3}	2.41×10^{-4}	2.54×10^{-5}
Ar	5.25×10^{-7}	1.39×10^{-9}	2.65×10^{-3}	2.23×10^{-3}	9.12×10^{-4}
Kr	3.41×10^{-5}	1.16×10^{-7}	3.39×10^{-3}	3.38×10^{-3}	3.30×10^{-3}
Xe	3.53×10^{-4}	6.4×10^{-8}	1.81×10^{-4}	1.81×10^{-4}	1.81×10^{-4}

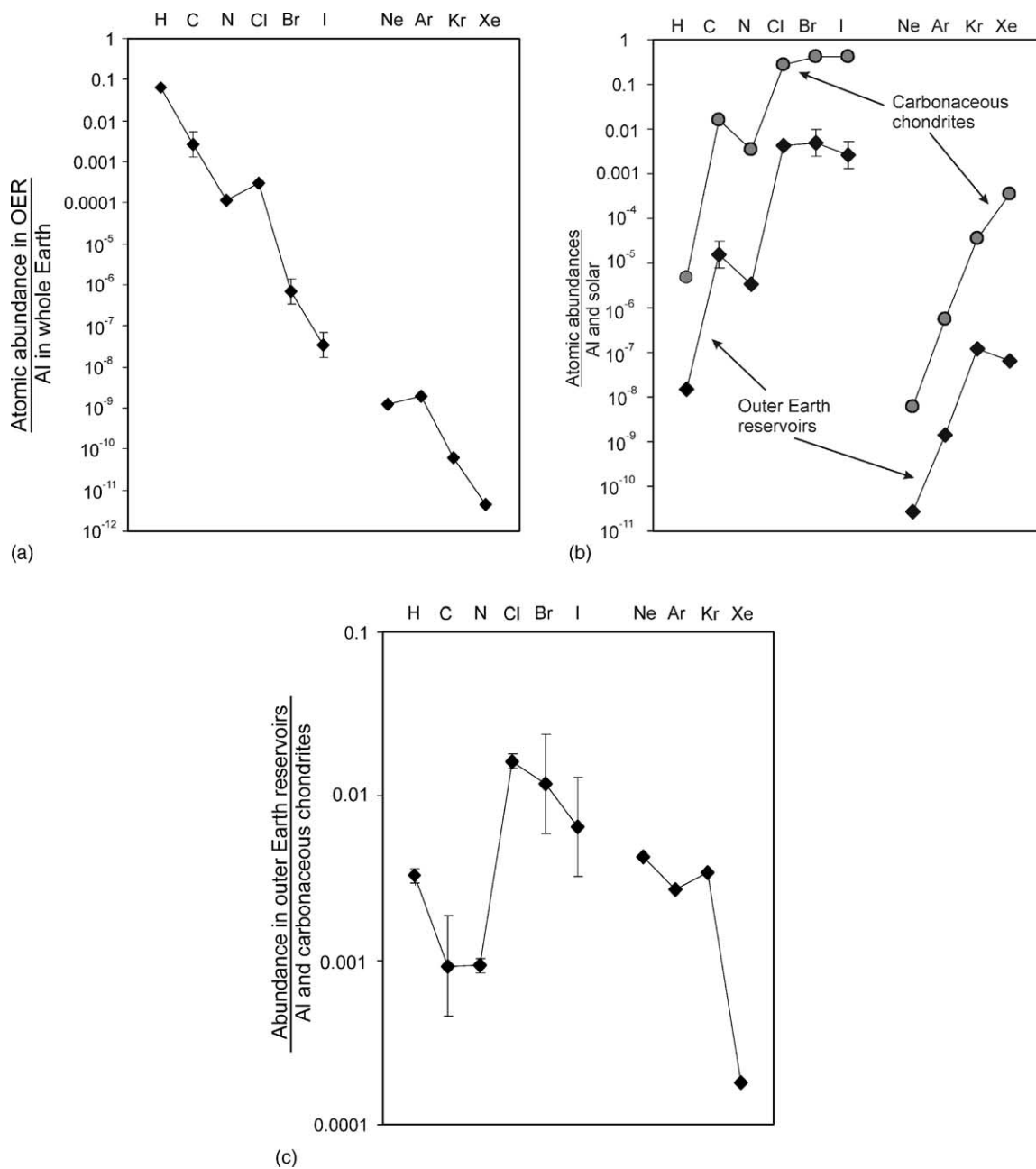


Fig. 1. Volatile element abundances (atomic) in the outer Earth reservoirs (OER, i.e. atmosphere, oceans, continental crust and MORB-source mantle) compared to various other reservoirs. Reactive elements and noble gases arranged separately in order of atomic weight. For data sources, see Table 1. (a) Element abundances in OER normalized to Al in the whole Earth. (b) Abundances as in (a) (black diamonds) and Al-normalized atomic abundances in average carbonaceous chondrites (CC, grey circles), both relative to Al-normalized atomic abundances in solar matter. (c) Abundances in OER as in (a) and (b), normalized to abundances in CC as in (b).

for two reasons. First, available isotope evidence, discussed below, indicates that volatile elements in the lower mantle do not represent recycled atmosphere. Second, the amounts of many volatiles in them are unknown. For instance, significant C may reside in the core (Wood, 1993) and the lower mantle may have a high nitrogen content (Tolstikhin and Marty, 1998). For the noble gases, the OER budgets are essentially the present atmospheric ones. For the other elements, MORB-source mantle contributions to the OER budget are briefly annotated below.

2.1. Hydrogen

The depleted mantle appears to have a H₂O content between 100 and 500 ppm, with the N-MORB source probably closer to 100 ppm (Sobolev and Chaussidon, 1996). This value range is consistent with the amount of OH detected in nominally anhydrous minerals in mantle derived xenoliths (Bell and Rossman, 1992), and corresponds to 11–55 ppm H. Thus, the amount of hydrogen in the depleted mantle is between about 1 and 7 ppm of the Earth. Isotope data show that this mantle hydrogen represents a mixture of recycled water from the surface, and juvenile water or hydrogen: While plume volcanism has a δD value of $-80 \pm 10\%$, that of the MORB-source mantle is heterogeneous, between -40 and -80% (see Lécuyer et al., 1998). Thus, the mantle contribution to the OER hydrogen budget is relatively small, but generates most of its uncertainty (Tables 1–3, Fig. 1).

2.2. Carbon

Unlike the case for H, The mantle-recycled component of C in the terrestrial budget is probably very important. Marty and Tolstikhin (1998) have calculated 37 ± 23 ppm from CO₂/Ar and CO₂/He ratios in MORB. This value is consistent with the lower end of the plausible C content range (40–80 ppm) obtained for the MORB source from thermodynamic modeling (Holloway, 1998). If the mass of the depleted MORB-source mantle is 1.4×10^{27} g, the amount of C it contains is about equal to that in the present day crust (see footnotes to Tables 1–3). Important mantle recycling of C is also expressed in the uniform $\delta^{13}C$ value of -5.2% in the MORB-source mantle (Marty and Zimmermann, 1999), which is equal to the

weighted average of carbonatic and organogenic carbon (Schidlowski, 2001). Primeval “juvenile” mantle C is likely to have a lighter isotope composition. The $\delta^{13}C$ values down to -25% have been reported for diamonds (Cartigny et al., 1998, 2001). While these have been attributed to subducted organogenic C or, alternatively, to fractionation (Cartigny et al., 2001), a primeval light mantle carbon is not discounted.

2.3. Nitrogen

Studies of MORB have allowed the C/N ratio of the MORB-source mantle to be constrained at 530 ± 230 (Marty and Tolstikhin, 1998) assuming incompatible behavior of nitrogen in mantle melting (but see Javoy, 1998; Cartigny et al., 2001 for an alternative view). This indicates rather insignificant mantle recycling of N. In accordance with this is a considerable N isotope heterogeneity observed even in MORB, with $\delta^{15}N$ values down to -10 and averaging -3.3 (Marty and Zimmermann, 1999). This probably reflects mixing of a small recycled component with isotopically much lighter primeval N. The latter is observed in diamonds, which have heterogeneous $\delta^{15}N$ values with a main population between -10 and $+5$, and a few values down to -25 (Cartigny et al., 1998).

2.4. Halogens

F has not been included as it is not a strongly incompatible element. For Cl and Br, mantle concentrations of 0.5 and 0.005 ppm are reported (Wänke et al., 1984). This may be in part recycled Cl and Br, but constitutes a mere 2% of the OER budget in both cases. For I, the amount in the MORB-source mantle (about 0.004 ppm, Wänke et al., 1984) is almost as great as in the ocean and crust combined. Either I is not as thoroughly degassed from the mantle as Cl and Br, or, more likely, it is recycled.

2.5. Conclusions

In spite of the uncertainties, a clear pattern emerges in Fig. 1a. H is in terms of atomic abundance by far the most abundant volatile element in the OER, and for the major volatiles, the smooth decrease with atomic mass is only broken by anomalously abundant Cl. The noble gases are all around four orders of magnitude less

abundant than major volatiles of comparable atomic mass.

3. Solar- and carbonaceous chondrite-normalized abundances of major volatiles

In Fig. 1b, the Al-normalized OER abundances relative to the mass of the whole Earth (OER/TE) and of an average of CC types are shown normalized to Al and solar matter. At first sight the similarity of these solar-normalized patterns for the OER/TE to those for CC is striking, with the OER/TE between 2 and 3.5 orders of magnitude depleted relative to the CC whereas depletions relative to the solar values vary by six orders of magnitude for the major volatiles. Volatile abundances of the OER, normalized to CC, are listed in Table 3 and shown in Fig. 1c. Deviations from chondritic relative abundances are much more obvious in Fig. 1c than in Fig. 1b due to the narrowing down of the scale.

For an abundance ratio of volatile elements, the N/C ratio is rather uniform among chondrite groups other than enstatite chondrites, around 0.05 and varying not more than a factor 3, while C and N concentrations vary two orders of magnitude (Wasson and Kallemeyn, 1988). This is probably due to the fact that C and N exist in chondrites in similar types of compounds, mainly hydrocarbons. The ratio is only a factor 4 lower than solar; the much lower ratio in enstatite chondrites is probably related to the very reduced character of the parent body, leading to incorporation of C in the metal phase before loss of the volatile components. The N/C ratio of Comet Halley (Altwegg and Balsiger, 1999) and Comets Hyakutake and Hale-Bopp (Crovisier and Bockelée-Morvan, 1999) are also in the range of those of CC and ordinary chondrites.

The N/C ratio of the OER appears to be close to chondritic, as are the atmospheres of Venus and Mars (Prinn and Fegley, 1987, Lécuyer et al., 2000). On Venus, surface temperatures are above those of carbonation reactions even at 90 bar CO₂ pressure (Sleep et al., 2001 and references therein), so that resurfacing events cannot transport carbon back into the interior, which is thought to be strongly degassed by volcanism. Therefore, the C/N ratio of the atmosphere of Venus is essentially that of its mantle before degassing. On Mars, a significant fraction of CO₂ resides in the polar

ice caps, which may account for a somewhat higher atmospheric N/C ratio. Overall, in spite of the uncertainties (particularly concerning the Earth) and the highly volatile character of C and N, the N/C similarities between the OER, Venus, Mars and CC are remarkable.

While Al-normalized H is depleted in CC by 5×10^{-6} relative to solar matter (Fig. 1b), the halogens have almost solar abundances. In view of this huge difference and the different compounds in which these elements occur on Earth and in the CC, the almost chondritic relative H, Cl, Br and I abundances of the OER are striking. Notwithstanding the offset of N and C relative to H, Cl and Br, the major volatile abundance pattern of the OER is vastly more similar to CC than to solar matter.

4. Noble gas abundances and isotopic constraints

The noble gas budget of CC is complex and consists of distinct components. Broadly, however, their overall abundance pattern with relative depletion of the light gases, or enrichment of the heavy ones, probably reflects early mass-dependent fractionation processes in the nebular atmosphere and during CC formation. These are also expressed in isotope fractionation (e.g. Ozima et al., 1998).

The noble gases Ne, Ar (primeval Ar only), and Kr in the OER appear at first sight to have a chondritic abundance pattern, but the notion that terrestrial noble gases could have been derived from CC-like material encounters very serious paradoxes. One of these is the great relative deficiency in Xe, which is coupled with a strong isotope fractionation, depleting the light isotopes by several percent relative to CC and solar values (e.g. Pepin, 1991). A further one is a solar, rather than CC, isotope signature of Ne in the deep mantle.

The missing Xe problem has not been solved. The relative depletion, coupled with the isotope fractionation, points strongly to loss from the atmosphere by hydrodynamic escape as modeled by Pepin (1991). Such a process leads to mass fractionation (Zahnle and Kasting, 1986) and is discussed later in this paper. The problems are that Xe is depleted relative to the lighter noble gases, and that it is isotopically more fractionated than the lighter Kr, making it highly unlikely that Xe and Kr were lost from the atmosphere in the same

event. A solution suggested by Tolstikhin and O’Nions (1994) and Zahnle (1994) is that Xe could be degassed from a planetary interior in preference to other noble gases, being less soluble in silicate melts (Lux, 1987; Shibata et al., 1998). Therefore, it could have been lost in very early processes, before the lighter gases were in the atmosphere or atmospheres concerned: the missing Xe problem may point to pre-accretion degassing, and is not further addressed in this paper.

The Ne isotope problem is more straightforward. While the atmospheric $^{20}\text{Ne}/^{22}\text{Ne}$ ratio is 9.8, values up to 13 are found in volcanic rocks (Honda et al., 1991; Hiyagon et al., 1992; Ozima and Igarashi, 2000). This is still below the solar wind value of ca. 13.8, but well above the “Q” gas component value of ca. 10.8 which dominates noble gases in most chondrites (Ozima et al., 1998). Values of 12.5 for the most retentive Ne fractions in rocks from the Iceland and Loihi plumes (Trieloff et al., 2000) are similar to those of the early solar wind component found in meteorites (Black and Pepin, 1969). This shows clearly that a solar component was introduced into the Earth. The difference in Ne isotope ratio between this suggested primeval component and the atmospheric one is well within the range of fractionation expected in atmosphere loss (Hiyagon et al., 1992). The isotope arguments for a solar component may extend to Ar (Kunz, 1999).

5. Possible sources of terrestrial volatile elements

The sources to be discussed include (1) material similar to CC, (2) comets, delivered over geological time, (3) a captured solar atmosphere or (4) pre-accretion solar wind.

From Sections 2 and 3 it follows that, while the major volatile element abundance pattern supports the notion of a source similar to CC, the noble gas pattern and isotope ratios cannot readily be reconciled with this: Ne and possibly Ar isotopes require a predominantly solar-type source while the missing Xe problem may point to a pre-accretion loss process. With these caveats, a CC-like source is nevertheless discussed below.

A source material for the Earth similar to CC has been advocated on the basis of chemical similarities by many authors, most recently Allègre et al. (2001). For

the whole Earth this is somewhat unlikely for several reasons. First, CC have generally less than 5% metal, whereas the Earth has a metallic core 32% of its mass. Second, the evidence for a light element in the core (possibly Si or C) further indicates extremely reducing conditions of metal formation in the terrestrial feeding zone, or core formation in the Earth. This is in contrast to the more oxidized environment of CC. Already at the inner rim of the asteroid belt, enstatite chondrite material, which is strongly reduced, occurs.

As planetary feeding zones become naturally depleted in planetesimals, it is unrealistic to expect classes of meteorites to exist that have the exact chemical characteristics as any given planet. Some type of heterogeneous accretion model for the Earth as proposed by Wänke et al. (1984) and Dreibus and Wänke (1987) may satisfy observations on the major volatiles. The terrestrial source material during early Earth accretion is considered to be from the feeding zone close to our present orbit, and reduced. In later stages of Earth accretion the addition of a more oxidized component, similar to CC, is envisaged. This idea is made plausible by early solar system numerical simulations invoking a disturbance of orbits around the asteroid belt, or outside it, by Jupiter (Chambers and Wetherill, 1998; Morbidelli et al., 2000). The asteroid belt appears to be dominated by material similar to CC (Meibom and Clark, 1999).

There are several reasons to assume that in early accretion, a volatile-poor Earth would have been formed. C might readily be incorporated in metallic melts before or during accretion or in the growing planet (Wood, 1993) and H_2O , consumed by reaction with metallic melt, would give rise to H_2 which could thermally escape to space. Further, the lower gravity of the smaller planet or its precursors would facilitate hydrodynamic escape even of heavy molecules (discussed in Section 7) and allow impact erosion of any atmosphere that formed.

If the early accreting matter (at least its silicate portion) was essentially devoid of the major volatile elements H, C and N, and possibly Cl and Br, and late accreting matter contained an important CC-like component, a broad similarity of the OER major volatile element pattern with that of CC would indeed be expected. Under the postulated more oxidizing conditions of late accretion, major incorporation of C into metal is unlikely at this stage and the near-chondritic

and near-solar C/N ratio of the OER can be explained in this way. However, the underabundance of both C and N relative to H and the halogens, as well as the noble gas observations, mean that the CC-source hypothesis is still untenable in its simple form.

The hypothesis that comets have, over geological history, delivered most or even all of the Earth's atmosphere (Owen and Bar-Nun, 1995) is popular, but there are decisive arguments against comets being a significant source for terrestrial water. First, the D/H ratio of comets measured so far (which are all Oort Cloud comets) is twice that of OER water (Balsiger et al., 1995; Bockelée-Morvan et al., 1998; Eberhardt et al., 1995; Meier and Owen, 1999; Meier et al., 1998a,b). Second, the C/H and N/H ratios of comets are similar to those of CC (Altwegg and Balsiger, 1999; Crovisier and Bockelée-Morvan, 1999; Huebner and Benkhoff, 1999), i.e. about 4× higher than those of the OER. Thus, any significant cometary replenishment of OER water would have caused much higher C/H and N/H ratios in the OER than observed. Possible H escape following CH₄ photolysis during the first half of Earth history (Catling et al., 2001) would further aggravate this problem. Although no D/H, C/H or N/H measurements have yet been made for Kuiper Belt comets, these constitute a minor population and thus it seems unlikely that comets have added significantly to the terrestrial water budget.

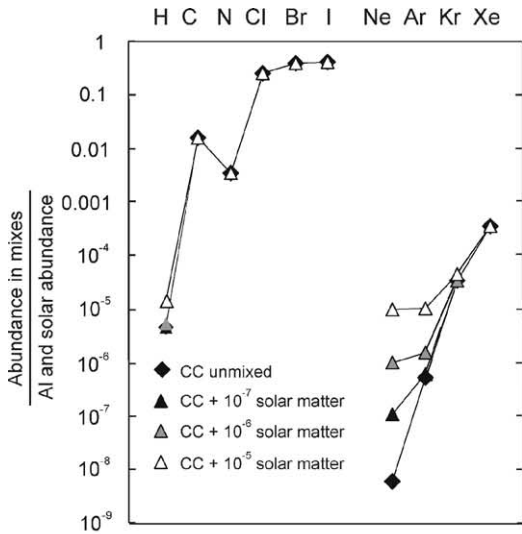
The N/H and C/H argument naturally applies to CC material as much as it does to comets. However, the CC hypothesis applies to accretion and leaves latitude for differential loss models such as discussed in Sections 6 and 7, while delivery of volatiles by comets would occur over geological time, and no episodes of massive volatile loss that could have modified these element ratios are thought to have occurred after the very early Archean.

The Ne isotope data require that the Earth's volatile element budget has a solar component. This could be a remnant of an atmosphere of solar composition, which represented nebular gas originally captured by gravity, or it could have been introduced by solar wind irradiation of pre-accretion solid matter (Ozima and Zahnle, 1993; Podosek et al., 2000). Neither scenario is likely to have resulted in a very major contribution. The scenario of atmosphere capture would require that much nebular gas still existed in the accretion disk at a

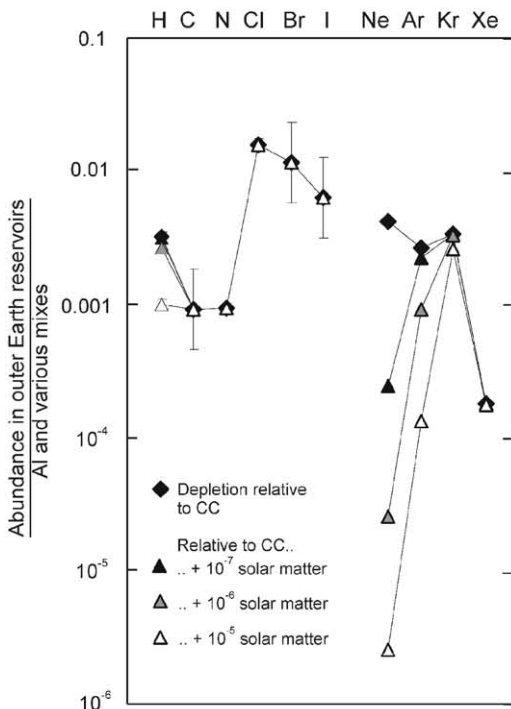
time when the Earth had grown to close to its present size (at least 30 million years after chondrite formation, Chambers and Wetherill, 1998; Schoenberg et al., 2002; Yin et al., 2002). This is unlikely. Podosek and Cassen (1994) have estimated a lifetime of ca. 10 Ma for dense dust in the solar nebula. As gas entrains dust, the lifetime for nebular gas is expected to be similar. Further, the probability that any subsequent process of differential loss, starting from a solar composition, with depletions between 10⁻¹¹ and 10⁻² for the different elements, would have resulted in a relative abundance pattern so similar to that of CC is extremely small. However, a small solar component introduced by either mechanism is not excluded.

To show the effect of such a solar component on the OER element budget, OER/TE volatile element abundances normalized to CC, with small admixtures of solar matter, are listed in Tables 1–3. The solar-normalized patterns of the CC-solar mix and the mix-normalized patterns of the OER are shown in Fig. 2a and b. Varying the source mixture naturally has the greatest effect in the case of elements that are most strongly depleted in CC relative to solar matter. Even a very small admixture of solar matter ($A_{\text{solar}}/A_{\text{total}} = 10^{-7}$) makes this the dominant contributor of Ne to the Earth, reconciling the mantle Ne isotope data, and changes the OER depletion factor for Ne by an order of magnitude. Of the volatile major elements, H depletion in the OER begins to be significantly affected at a solar component of 10⁻⁵, C and N at 10⁻² (not shown) and the halogens would remain hardly affected even if the source is a 1:1 mixture. In summary, it appears that CC-type material, spiked with an amount of solar matter which essentially changes the Ne abundance only, could make an appropriate source for major terrestrial volatiles as well as noble gases. Problems remaining are the missing Xe paradox, which is not addressed here, and the underabundance of C and N relative to H and the halogens, which will be discussed in Sections 6 and 7.

Volatiles from accreting planetesimals would have entered the atmosphere by magma degassing, either immediately following impact, or, more likely, through volcanism. Thereby the mix of major volatiles (H₂O, CO or CO₂, N₂) would exsolve as bubbles, and trace volatiles (such as noble gases) would partition into these (Lux, 1987; Kramers and Tolstikhin, 2000). As gravitational heat from core formation alone would



(a)



(b)

Fig. 2. The atomic abundance of volatile elements: (a) Al-normalized volatile element concentrations in average carbonaceous chondrites (CC) and in mixes of CC with various small additions of solar matter, normalized to solar abundances. Mix ratios are expressed as $A_{\text{solar}}/A_{\text{CC}}$. For data sources, see Table 1. (b) In the outer Earth reservoirs (OER), normalized to the Al abundance in the whole Earth, normalized to CC and CC-solar mixes of (a).

have been $\sim 3\times$ the total radiogenic heat produced throughout Earth history (Flasar and Birch, 1973), magmatic processes must have been extremely active, leading to a rapid release of volatiles into the atmosphere in the syn- and immediately post-accretionary Earth.

6. Constraints on atmosphere loss

The overall depletion in the OER volatile abundance pattern compared to that of CC could reflect volatile loss, or a small proportion of late accreting CC-like material, or a combination of both. This depends on the amount of the suggested relatively late CC-type contribution to the Earth, which remains unknown and cannot be well constrained by these data. Nevertheless there are several lines of evidence which indicate that large losses of volatile elements have occurred from accreting bodies and/or the planet itself, in various stages of accretion, and after accretion. These derive from the abundance pattern itself, and from radiogenic Xe.

Against the background of the much greater fractionation relative to solar matter, the broad similarity between the OER relative volatile element abundance pattern and that of average CC has been used above as an argument for a CC source of terrestrial volatiles. Nevertheless there are quite clear variations in the CC-normalized OER pattern, notably (1) the greater depletion of C and N compared to H, Cl and Br, and (2) (if a solar component from irradiation/implantation is invoked to explain Ne isotope characteristics) the greater depletion of Ne relative to primeval Ar and Kr. Further, as discussed in Section 2, H, C and N also appear to be isotopically fractionated in the OER relative to terrestrial samples of deep provenance, with depletion of the lighter isotope. These observations point to a process of atmosphere loss in which the lighter molecules were preferentially lost.

While the difficult problem of missing common Xe (which could have been lost well before accretion) is not addressed here, there are two radiogenic isotopes of Xe for which the production in the Earth, or accreting planetesimals, is known with reasonable confidence. These are ^{129}Xe , the daughter of ^{129}I (half-life 15.7 Ma), and ^{136}Xe , produced by spontaneous fission of ^{244}Pu (half-life 80 Ma). The initial abundances of

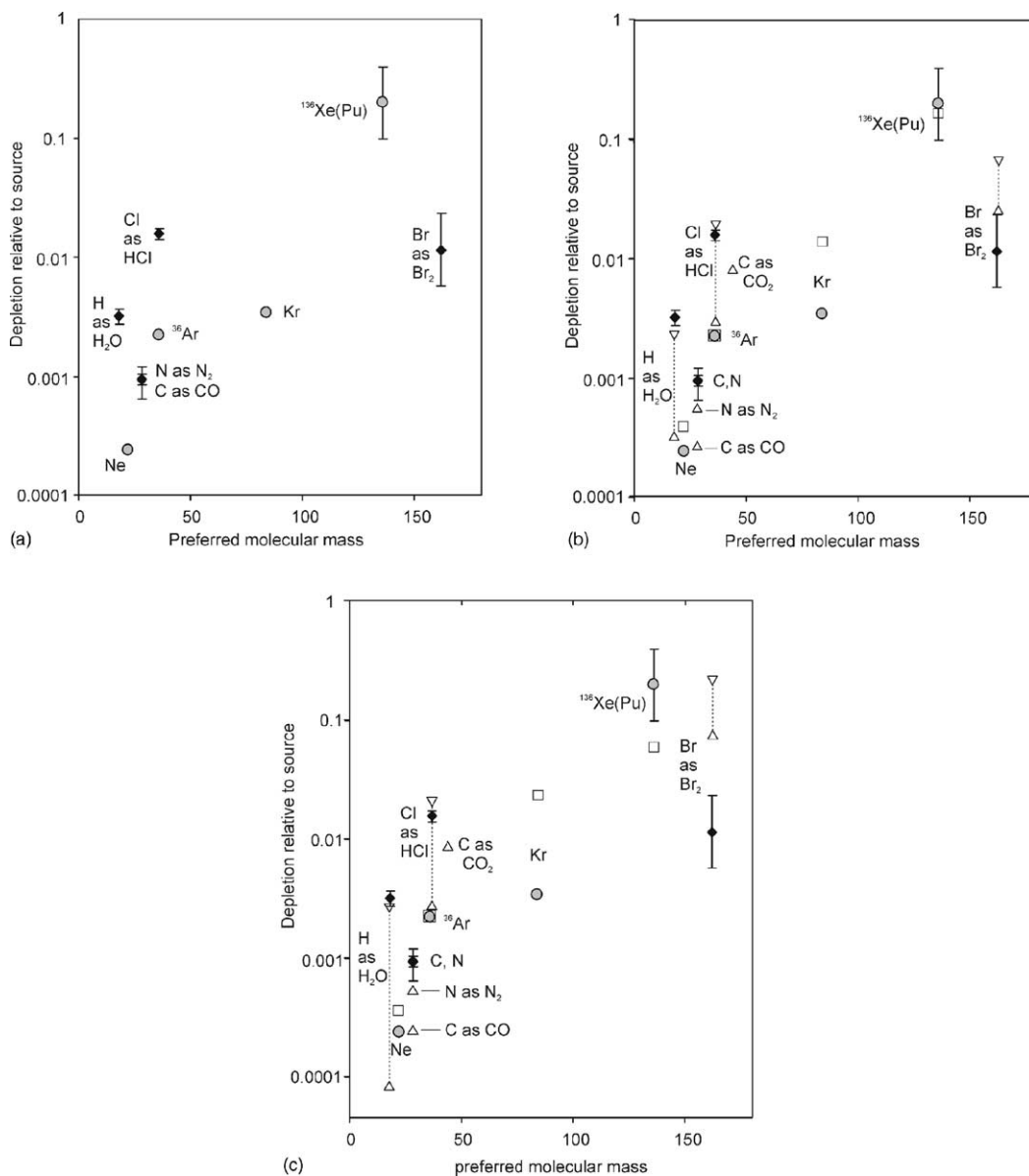


Fig. 3. Data, assuming as source a mix of average CC with 1×10^{-7} (Al/Al) addition of solar matter implanted, and depletions found from modeling. (a) Data. Grey circles: noble gases; black diamonds: other elements. $^{136}\text{Xe(Pu)}$ is shown instead of common Xe, as its loss from the Earth is much better constrained. (b) Data as in (a) and results of modeling of gas loss by hydrodynamic escape using the algorithms of Zahnle and Kasting (1986) in two stages. Open squares: Noble gases. Open upright triangles: other elements. Inverted triangles for H, Cl and Br: results of modeling with a liquid water ocean. The mixed volatile source is assumed to constitute 10% of the mass of the Earth, i.e. initial abundances for all elements are 0.1 (except for $^{136}\text{Xe(Pu)}$, for which it is 1). Parameters for modeling: first stage, relative Ar depletion to 0.3; H_2 flux 1×10^{13} molecules $\text{cm}^{-2} \text{s}^{-1}$. Second stage, total relative Ar depletion taken to 0.023 (i.e. 0.0023 of the mixed volatile source); H_2 flux 3×10^{13} molecules $\text{cm}^{-2} \text{s}^{-1}$. In the first stage, gases heavier than Ar and HCl are not depleted. For both stages: $T = 300 \text{ K}$; 30% of H_2O and 35% of HCl and Br_2 are assumed to be in the atmosphere. (c) As (b), but the mixed volatile source is assumed to be 100% of the Earth. Ar depletions are 0.3 after the first stage and a total of 0.0023 at the end of the second stage. $T = 300 \text{ K}$; 40% of H_2O and 60% of HCl and Br_2 are assumed to be in the atmosphere.

the parent isotopes are reasonably well constrained (Brazzle et al., 1999; Eugster et al., 1993; Hagee et al., 1990; Hudson et al., 1989). From the I content of the Earth and its present abundance of ^{136}Xe in the atmosphere, it can be estimated that $\sim 99\%$ of $^{129}\text{Xe}(\text{I})$ has been lost. Strong geochemical affinity of Pu with Nd allows the initial abundance of ^{144}Pu in the Earth to be estimated, and this leads to the conclusion that between 60 and 90% of $^{136}\text{Xe}(\text{Pu})$ has been lost. I–Xe systematics on their own merely constrain a minimum time interval for atmosphere loss of ca. 90 M after formation of the solar system. However, the 80 Ma half-life of ^{144}Pu means that significant production of $^{136}\text{Xe}(\text{Pu})$ continued after accretion was complete. Indeed, $^{136}\text{Xe}(\text{Pu})$ is found in the mantle (e.g. Kunz et al., 1998), and the combined $^{129}\text{Xe}(\text{I})$ – $^{136}\text{Xe}(\text{Pu})$ systematics indicate that loss of Xe took place until 100–200 million years after the formation of chondrites (Azbel and Tolstikhin, 1993). As Xe is a heavy gas, this means either bulk atmosphere loss without strong mass-dependent fractionation, or a much more massive loss of lighter gases than the 60–90% estimated for $^{136}\text{Xe}(\text{Pu})$.

It can thus be concluded that loss of atmosphere from the Earth must have occurred. Differing scenarios exist for this. Loss of bulk atmospheres as a consequence of antipodal ground movement during a giant impact such as formed the Moon (Chen and Ahrens, 1997) is rendered less likely by later work (Genda and Abe, 2002) and is still an open question. Atmospheric erosion in medium size impacts appears to be unlikely for planets the size of the Earth (Newman et al., 1999), although it could have occurred on Mars (Melosh and Vickery, 1989).

Hydrodynamic escape would however be a viable mechanism for atmosphere loss, even at our planet's mass. In this process, the loss to space results from thermally escaping molecules (predominantly H_2) colliding with heavier ones, causing a "drag flux" of these heavier molecules. The process would cause preferential loss of lighter elements, as well as isotope fractionation (Zahnle and Kasting, 1986). In a hierarchical accretion history (Chambers and Wetherill, 1998) total volatile loss could include impact atmosphere erosion at early stages and hydrodynamic escape at late stages. The hydrogen required for hydrodynamic escape could have been produced by UV photolysis in the upper atmosphere or by reaction

of a steam atmosphere with metal following a large impact (Pepin, 1997).

In a first assessment, the OER abundances of the noble gases Kr, Ar and Ne, together with the major volatiles N (as N_2) and C (as CO) portray a reasonably coherent pattern of mass-dependent depletion, particularly if a solar component of at least 5×10^{-8} is assumed to reconcile the Ne isotope data: the lighter molecules are most depleted (see Figs. 1c and 3a). H and Cl (for which the main degassed molecules are H_2O and HCl) do however not fit this pattern. As noted above, the relative overabundance is particularly striking for H, which forms a light molecule and should therefore be more depleted than C. It is remarkable that of the two clearly overabundant elements, one forms a liquid under ambient conditions (H as H_2O) and the other is extremely soluble in that liquid (Cl as HCl).

A possible explanation for the H and Cl overabundance is offered by the working hypothesis that throughout most of early atmosphere loss on the Earth and maybe even its precursors, a large portion of H was not in the atmosphere, but existed as a liquid water ocean and/or ice, so that the proportion of H_2O vapor in the atmosphere was always much smaller than that in the OER as a whole. As loss of a gas from the atmosphere is proportional to its abundance there, this would lead to a smaller loss. As C (probably mainly as CO) and N (as N_2) were wholly in the atmosphere, their mass-dependent loss in proportion to their total abundance would be predicted. The observation that Cl is considerably less depleted than C and N would then indicate that this ocean was most often liquid, rather than frozen. The working hypothesis is not contradicted by radiative–convective modeling of a massive CO_2 atmosphere on the early Earth (Kasting and Ackerman, 1986; Kasting, 1993), which would allow liquid water to exist on the very early Earth in spite of a ca. 30% weaker sun.

7. Estimation of volatile element depletion by hydrodynamic escape

In hydrodynamic escape, general parameters determining the drag escape flux are the H_2 flux itself, the altitude of the exosphere or top of the atmosphere, where escape occurs (i.e. radius from the planet center), and the mass of the planet. Specific parameters

for a given species of molecule are its molecular mass and its binary diffusion coefficient in the fluxing gas: the greater the molecular mass or the lower the diffusion coefficient, the smaller the rate of escape.

Hydrodynamic escape thus leads to element fractionation (as well as isotope fractionation) according to molecular weight. Further, a molecule's escape rate is proportional to its abundance N in the atmosphere. The ratio of the escape flux of one molecule species (i) relative to another (s) is thus

$$x_{is} = \frac{\varphi_i/N_i}{\varphi_s/N_s} \quad (1)$$

For the chemical or isotopic evolution of an atmosphere undergoing hydrodynamic gas loss, x_{is} is a fractionation factor:

$$\frac{(N_i)_t}{(N_i)_0} = \left(\frac{(N_s)_t}{(N_s)_0} \right) x_{is} \quad (2)$$

where t and 0 refer to situations after and before the gas loss. For the realistic case of a transonic escape flux, Zahnle and Kasting (1986) have developed algorithms which allow approximation of x_{is} with s denoting H_2 . Thereby an important parameter is Φ_i , the ratio of factors favoring escape to those inhibiting it (equation 22 of Zahnle and Kasting, 1986):

$$\Phi_i = \frac{\varphi_s r^2 k T}{m_i G M b_{si}(T)} \quad (3)$$

Here r is the altitude (radial distance from the center of the planet) of the exosphere, and T the temperature in this zone; m_i denotes the molecular mass of i and b_{si} its binary diffusion coefficient in medium s . G is the gravitational constant and M is the mass of the planet. In the calculations for x_{is} (equations 35 and 36 of Zahnle and Kasting, 1986) parameter Φ_i appears in the denominator of the most important terms. Therefore, a stronger H_2 flux, lower gravity, greater altitude of the top of the atmosphere and higher temperature all lead to smaller mass fractionation.

Relative depletions were calculated using the method of Zahnle and Kasting (1986), starting from a mix of 1 part CC + 1×10^{-7} part solar matter (see Table 2). To transform sets of relative depletion factors into depletion patterns for elements i , the depletion of Ar was set to a given value and values

$N_i(t)/N_i(0)$ were determined by

$$\frac{N_i(t)}{N_i(0)} = \left(\frac{N_{\text{Ar}}(t)}{N_{\text{Ar}}(0)} \right)^{x_i/x_{\text{Ar}}} \quad (4)$$

The modeling was aimed at reproducing three principal observed features described in Section 5: (1) the apparent strong depletion of C, N and Ne relative to Ar, (2) the depletion in $^{136}\text{Xe}(\text{Pu})$, and (3) the overabundance of normalized H (as H_2O) relative to C and N, and Cl (as HCl) relative to Ar.

Reconciling the observed strong fractionation of the light gases (Figs. 1c and 3a) requires hydrodynamic escape with a H_2 flux of the order of 1×10^{13} molecules $\text{cm}^{-2} \text{s}^{-1}$ from the exosphere. In such a scenario, however, gases with a molecular mass greater than ~ 40 are not lost from the atmosphere. While considerable $^{129}\text{Xe}(\text{I})$ loss may have been pre-terrestrial, the depletion of $^{136}\text{Xe}(\text{Pu})$ to about 10–40% occurred from a completely accreted Earth. $^{136}\text{Xe}(\text{Pu})$ depletion was therefore included in the modeling (Fig. 3b and c) instead of common Xe or $^{129}\text{Xe}(\text{I})$. To achieve the observed amount of depletion of $^{136}\text{Xe}(\text{Pu})$ without complete loss of lighter species in the atmosphere, extremely large H_2 fluxes in the order of 3×10^{13} molecules $\text{cm}^{-2} \text{s}^{-1}$ are required, yielding very high values of Φ_i and low values of x_i . Such a large H_2 flux is however incapable of producing the observed strong fractionation between Ne, C, N and Ar. Incidentally, it could also not produce the fractionated Xe isotope pattern seen in the atmosphere. In this respect, the present approach is very different from that of Pepin (1991), in which the Xe isotope fractionation was one of the starting points.

These requirements can be reconciled if it is assumed that the H_2 flux was variable during the escape process, which might have been episodic or continuous. For the purpose of modeling two stages were assumed, one with 1×10^{13} molecules $\text{cm}^{-2} \text{s}^{-1}$, and another one with a H_2 flux of 3×10^{13} molecules $\text{cm}^{-2} \text{s}^{-1}$. Ar depletions in the two stages were set to yield a total depletion of either 0.00223 (see Table 3) or 0.0223, for the case of CC having formed 10% of the Earth (Fig. 3). While it is thus assumed that the H_2 flux in hydrodynamic escape was somehow bimodal, this two-stage modeling does not imply that atmosphere depletion actually happened in two episodes. The data or algorithms do not impose an order of events. Either of the “stages” could have occurred first, or the

scenarios could have alternated. Further, a large H₂ escape flux is not necessarily synonymous with a large overall depletion, as the duration of the process is unconstrained.

The results are shown in Fig. 3b and c, with initial volatile budgets in the Earth equal to 0.1 × mix, and 1 × mix, respectively (the first scenario corresponds to CC-type meteorites making up 10% of the Earth). It is seen that in either case, the observed abundances for species with molecular mass up to 40 can be reproduced fairly well. In particular, the depletion of Ne and N relative to primordial Ar is easily reproduced, as also noted by Zahnle and Kasting (1986). The calculated depletion is too great for C as CO, but this discrepancy can be reconciled if a portion of C existed as CO₂ during atmosphere loss. Overall, a more comfortable fit is achieved for the first (10%) scenario than for the second (100%) one.

The effect of a liquid water ocean, assumed to address the overabundance problem for H and Cl (and Br), was simulated by assuming constant “Atmosphere fractions” F_i for elements partly residing in the ocean: H (as H₂O), Cl (as HCl) and Br (tentatively, as Br₂). $F_i = N_i(\text{atmosphere})/N_i(\text{total})$. The escape flux of these elements following Eq. (1) is then reduced by the factor F_i and the depletion factor can be corrected by

$$\begin{aligned} \left(\frac{N_i(t)}{N_i(0)} \right)_{\text{corrected}} &= N_i(0) e^{C_i}, \quad \text{where } C_i \\ &= F_i \times \ln \left(\frac{N_i(t)}{N_i(0)} \right)_{\text{uncorrected}} \end{aligned} \quad (5)$$

In this way the abundances found for H and Cl are reconciled by assuming a proportion of 50–70% of these (as H₂O and HCl, respectively) in the liquid water ocean during the escape episodes (F_i varying between 0.3 and 0.5, see Fig. 3). Depending on the scenario, H₂O is one to two orders of magnitude less depleted than it would be in the absence of a liquid water ocean. Zahnle and Kasting (1986) have treated this phenomenon from the opposite point of view, considering the greater potential loss of volatiles by hydrodynamic escape for a given water budget, if a liquid ocean was present. While the ocean effect on escape of Br (as Br₂) is not very obvious due to the uncertainties associated with its large mass, the solution of the combined H+Cl anomaly problem in the terrestrial volatile abundance pattern is obvious in Fig. 3b and c. For

such modeling of atmosphere depletion to yield the observed overabundances, it is essential that the 60–70% H₂O and 40–65% HCl “masking” in a liquid ocean occurs in both “stages”. Further, the figures arrived at are averages and it is not implied that a liquid ocean existed continuously: short-lived complete ocean evaporations upon large impacts are not excluded.

The massive loss of ¹³⁶Xe(Pu) must have occurred after, or continued until ~100–200 million years after the formation of the solar system (Azbel and Tolstikhin, 1993; Tolstikhin and Marty, 1998). This means that significant hydrodynamic escape with a very large H₂ flux must have occurred at this relatively late stage. A late, massive H₂ flux is difficult to explain by EUV radiation, which should have abated long before 200 million years. However, additional H₂ could be generated in a humid atmosphere by massive impacts of bodies containing reduced carbon, or metal (Pepin, 1997). An important requirement is, however, that early escape fluxes should not have depleted the H₂O budget of the planet. Assuming the quasi-continuous presence of an ocean containing ca. 60–70% of the Earth’s water even during the earliest episodes of hydrodynamic escape satisfies this constraint. Thus, the concept of an early water ocean not only helps to explain the present abundance of water on Earth, but also the observed loss of ¹³⁶Xe(Pu) and maybe part of the loss of ¹²⁹Xe(I).

It is of interest to see whether the amount of water lost from Earth could have produced the fluxes required, if partially lost as H₂. Assuming that 10% of the Earth accreted from CC material, the Earth lost about 30 × its present amount of H. This corresponds to ca. 3 × 10²⁹ molecules of H₂O or H₂ per cm² of exosphere. This total could sustain a flux of 10¹³ cm⁻² s⁻¹ for 10⁹ years. Thus, provided that there is a means of producing H₂ from H₂O, its availability imposes no constraints on the process envisaged.

Where H₂ is produced by EUV photolysis of H₂O, its escape leads to the existence of free oxygen in the atmosphere. Initially this would be used up immediately in the oxidation of CO to CO₂, thus providing the greenhouse effect required to keep the ocean from freezing (Kasting, 1993; Kasting and Ackerman, 1986). Further, C in the form of CO₂ can in pre-photosynthesis times be gradually removed from the atmosphere by direct carbonation reactions involving hydrous silicates (Sleep et al., 2001) or by subaerial

chemical weathering and erosion, followed by submarine carbonate precipitation (e.g. Kramers, 2002). A liquid water ocean, which would have enabled either of these processes, could have been the single most important factor to shape the Earth's environment from earliest times.

8. Summary and conclusions

In spite of the large uncertainties about the abundances of some volatile elements in the Earth, and the large range of volatile abundances in potential source material for the Earth, some robust observations can be made, and tentative conclusions drawn.

1. Against the background of the highly (by eight orders of magnitude) variable depletion relative to solar matter, the comparative similarity of the OER Al-normalized major volatile element abundance pattern to an average CC pattern is striking. Therefore, it is likely that the main source of major volatile elements on Earth was similar to CC.
2. Solar Ne isotope characteristics in the Earth's deep mantle can be explained by a small solar matter component in the accreting material. A relative proportion of $Al_{\text{solar}}/Al_{\text{total}} = 10^{-7}$ suffices to reconcile Ne isotope data, and does not affect the depletion abundance patterns for the major volatile elements. Another noble gas feature, the missing Xe and strong Xe isotope fractionation in the Earth, cannot be reconciled in this way.
3. Compared to such a solar-spiked CC-type source, Ne, N (as N_2), C (as CO) and primordial Ar in the OER display a coherent pattern of mass-dependent depletion. H and Cl do not fit this pattern. As H_2O and HCl, respectively, they should be about an order of magnitude more depleted than they are. The overabundance of H in the CC-normalized OER abundance pattern cannot be explained by addition of water by comet impacts over Earth's history, at least not comets from the Oort Cloud. First, cometary water is about $2\times$ deuterium-enriched relative to OER water, and secondly the C/H ratios measured in Oort Cloud comets are around $8\times$ higher than in the OER. This C/H argument also applies to a CC-type source, but in this case might be explained by early differential loss from the Earth.

4. The observed abundance pattern of the elements considered can be reasonably well approximated by calculations of hydrodynamic escape whereby H_2 escape fluxes varied from 10^{13} to 3×10^{13} molecules $cm^{-2} s^{-1}$. The smaller flux would cause relative fractionation of the lighter elements, whereas the greater flux would enable depletion of the heavier elements, required by Br, I and fissionogenic ^{136}Xe from Pu. If it is assumed that between 50 and 70% of H_2O and HCl resided in liquid water during this hydrodynamic loss, their overabundances can be reconciled.

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