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Noble gas signature of the Late Heavy Bombardment in the Earth's atmosphere

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Abstract. The Lunar cratering record is consistent with the occurrence of a late heavy bombardment (LHB), which marked the end of terrestrial planet accretion 3.8 billion years ago. However, clear evidence of a LHB on Earth has not yet been identified. Based on a volatile budget of the terrestrial mantle, the atmosphere and hydrosphere we propose that the LHB did indeed occur on Earth and that we are breathing its aftermaths. The terrestrial atmosphere and hydrosphere is enriched in noble gases relative to the abundance of volatiles in the mantle. This enrichment is consistent with the mass delivered to Earth during the LHB, as recently proposed from dynamical modelling (Gomez et al., 2005), if this material comprised a few Kuiper-belt (cometary) objets (KBOs) mixed in with a population of largely chondritic (i.e. asteroidal) impactors. The fraction of KBOs necessary to account for the atmospheric composition is, however, much lower ($<$1%) than the one ($\sim$50%) inferred from modelling.

1 Introduction

The lunar surface has preserved a record of the integrated flux of planetesimals in inner solar system because, contrary to the terrestrial planets (i.e. Mercury, Venus, Earth and Mars), there are no intrinsic geological processes operating on the surface of the Moon, which could have erased impact structures. Most giant craters on the Moon (e.g., Nectaris, Imbrium, Orientale) have ages that fall in a limited time-interval of $\sim$60 million years (Myr) about 3.85 to 3.80 billion years (Gyr) ago (Tera et al., 1974). Extrapolation of the impact size distribution and frequency on the Moon 3.8 Gyr ago to the earlier accretion period 4.0 to 4.4 Gyr ago yields an unrealistically high cratering rate and accumulated mass addition. This has led to the concept of a Late Heavy Bombardment (LHB), a short time span with a greatly increased flux of impactors in the inner solar system, against an otherwise exponentially decreasing background flux at the end of planetary accretion (Hartmann et al., 2000; Koeberl, 2006; Ryder et al., 2000; Tera et al., 1974).

Dynamical modelling (Gomes et al., 2005) of the orbital evolution of the solar system is now consistent with the lunar cratering record. Migration of the giant planets destabilized the orbits of objects residing beyond 15 AU in the Kuiper belt, and caused a sudden delivery of planetesimals and planetary bodies to the inner system. The simulations (Gomes et al., 2005) account for a number of key observations: (*i*) the characteristics of the Trojan asteroids (Morbidelli et al., 2005), (*ii*) the present-day orbits of the giant planets (Tsiganis et al., 2005), (*iii*) a delay of several hundreds of Myr after Solar system formation, and (*iv*) an estimated mass of material falling onto the Moon during the LHB of 8.4×10^{21} g, consistent with an independent estimate based on lunar crater sizes and ages: 6×10^{21} g (Hartmann et al., 2000). In the same process, the asteroid belt was also destabilized, so that the LHB flux of impactors to the inner solar system consisted of both cometary and asteroidal material (Gomes et al., 2005). A major unknown is the relative flux of asteroidal versus cometary materials to the inner solar system.

Delivered in a time-interval of less than 100 Myr, the effects of a contemporaneous bombardment of the Earth, the so-called terrestrial LHB (TLHB) would have been profound. Indeed, the TLHB would have resulted in $\sim$3000 impact structures with diameters larger than 100 km, with about 10 structures larger than the Imbrium basin on the Moon (1300 km in diameter) (Ryder et al., 2000). The entire surface of the Earth would have been affected both physically and chemically. An average of about 200 t/m^2 of extraterrestrial (ET) material would have been deposited, and major geodynamic changes (for example large scale perturbations of the plate tectonic cycle due to disruption of the crust) would have occurred. However, extensive searches for geochemical traces of the TLHB in the $\sim$3.8 Gyr old metasediments from the Isua (Greenland) supracrustal belt have led to inconclusive and contrasting results (Frei and Rosing, 2005;

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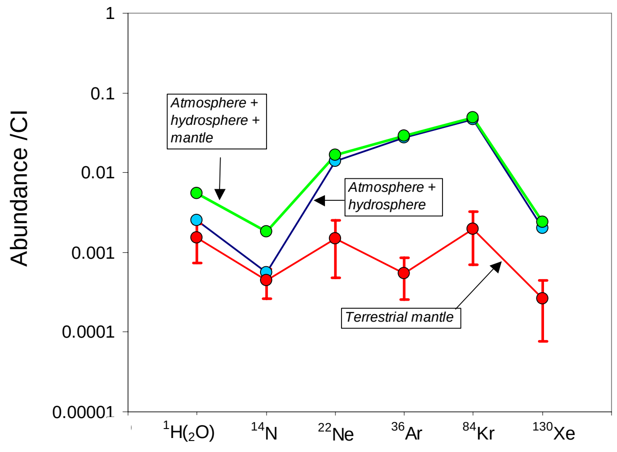

Fig. 1. Abundance of water, nitrogen and noble gases in the mantle and in the atmosphere (+ hydrosphere), normalised to CI composition. See text for sources of data.

Hartmann et al., 2000; Schoenberg et al., 2002). In this contribution, we suggest that the TLHB has left a signature in the composition of the atmosphere.

At the time of the TLHB, the mass and the composition of the atmosphere was already relatively constant because large-scale processes such as mantle degassing and mass-loss due to impact erosion or hydrodynamic escape were no longer considerable (Porcelli and Pepin, 2000; Tolstikhin and Marty, 1998; Zahnle, 2006). Xenon (Xe) isotope systematics indicate extensive mantle degassing and atmospheric escape in the first ~200 Myr (Staudacher and Allègre, 1982), and suggest that ≥98% of the volatiles initially trapped in the Earth were lost (e.g., Kunz et al., 1998; Tolstikhin and Marty, 1998; Yokochi and Marty, 2005). Thus, at the time of the TLHB, the Earth was poor in highly volatile elements and its composition sensitive to the contribution from volatile-rich bodies. The noble gas composition of the terrestrial atmosphere and mantle has previously been modelled by adding a cometary-like component to a fractionated atmospheric reservoir (Dauphas, 2003). In particular, Dauphas (2003) showed that adding a cometary component to an already isotopically fractionated (during early escape events) atmosphere yields noble gas isotopic compositions, including Neon and Xenon, which are fully consistent with the present-day atmospheric composition. We build on this work to quantify the contribution of cometary materials in the TLHB.

2 Normalized abundance of volatile elements in the mantle

Figure 1 displays an estimate of the mass of volatile elements in the terrestrial mantle, divided by the mass of the Earth and normalized to the corresponding mass-ratio in carbonaceous chondrites (CI). The choice of a chondritic composition for normalization is somewhat arbitrary at this stage and is used for the purpose of comparing reservoirs with drastically different compositions. The abundance of volatile elements in the mantle was established from (i) relationships between volatiles and more refractory elements (Marty, 1995; Saal et al., 2002), and (ii) volatile abundance data of mantle-derived samples, corrected for surface contamination and fractional degassing (Ballentine et al., 2005; Marty and Zimmermann, 1999; Moreira et al., 1998). The mantle water content is from from Bell and Rossman (1992) and Keppler and Bolfan-Casanova (2006) and cross-checked with Nb/H_2O and K_2O/H_2O relationships in mantle-derived rocks (Jambon and Zimmermann, 1990; Saal et al., 2002). Carbon was not included as there is no consensus in its abundance in the mantle. The nitrogen content was estimated from ^{40}K-^{40}Ar-N systematics of mantle-derived rocks (Marty, 1995; Marty and Dauphas, 2003). The rationale of the latter is that the major terrestrial reservoirs (mantle, crust, atmosphere) have comparable N/^{40}Ar ratios. Because ^{40}Ar is from the decay of ^{40}K , this relationship permits too link N and K, and to deduce a nitrogen content for the silicate Earth from the terrestrial potassium content (Marty, 1995). The total nitrogen content of the Earth is = 2.0±0.7 ppm computed with N/^{40}Ar$_{\mathrm{MORB}}$ ~N/^{40}Ar$_{\mathrm{OIB}}$ ~N/^{40}Ar$_{\mathrm{air}}$ ~160±40 (Marty and Zimmermann, 1999), and a terrestrial K content of 250 ppm. The mantle N/^{36}Ar ratio was determined from the mantle correlation between ^{40}Ar/^{36}Ar and N/^{40}Ar (Marty, 1995; Marty and Dauphas, 2003). The MORB and plume end-members have N/^{36}Ar ratios of $1.2\pm0.6\times10^{6}$ and $4.0\pm1.4\times10^{6}$, respectively. The mantle fraction of OIB-like material was allowed to vary between 5% and 20% following McDonough et al. (1992), and uncertainties were propagated accordingly. The ^{22}Ne/^{36}Ar/^{84}Kr/^{130}Xe abundance pattern of the mantle is adapted from Trieloff and Kunz (2005), taking into account MORB (Moreira et al., 1998), OIB (Trieloff and Kunz, 2005), and subcontinental mantle (Ballentine et al., 2005) data. Estimates were cross-checked using the ^{3}He flux – magma generation at ridges. The flux of ^{3}He from the depleted MORB mantle sampled at mid-ocean ridges is ~1000 mol/yr, for a lava production rate of 20 km^{3}/yr. For a mean partial melting rate of 12%, the ^{3}He content of the depleted mantle is 2×10^{-15} mol/g. With the ^{22}Ne content of the bulk mantle of 4.0×10^{-15} mol/g estimated from N-Ar systematics and noble gas patterns of the mantle, following the method outlined above and using a ^{3}He/^{22}Ne mantle ratio of 3–9 (Ballentine et al., 2005; Moreira et al., 1998; Yokochi and Marty, 2004), we obtain a ^{3}He bulk mantle content of $12\text{–}36\times10^{-15}$ mol/g, higher by one order of magnitude than the depleted mantle concentration. This difference reflects the integration of all mantle domains including volatile-rich regions like OIB sources. Note that mantle volatile concentrations have been assigned a factor of ~10 uncertainty (depicted in Fig. 1), thus taking into account possible mantle heterogeneities. The CI concentrations are from the compilation by Pepin (1991)

Figure 1 shows that the mantle volatile abundance pattern is approximately chondritic. This resemblance is consistent with the notion that volatile elements now in the terrestrial mantle are derived from asteroid-like (i.e. broadly chondritic) planetesimals. However, it does not imply that only chondritic material contributed mantle volatiles. Other sources like the solar nebula or solar wind gas implanted onto dust could have contributed some of the volatile elements like He or Ne. It has been proposed that solar Ne found now in the mantle was supplied by dust irradiated by the early Solar wind (Trieloff et al., 2000), thus accounting for the broad chondritic pattern for major and minor volatiles as well as for the Ne isotopic composition of mantle-derived samples. Notably, Fig. 1 shows that mantle volatiles are depleted by 3 orders of magnitude relative to CI, consistent with the conclusion that the mantle is a strongly degassed reservoir. A chondritic volatile inventory of a strongly degassed could be the result of mixing a completely degassed material with small amounts of pristine, unprocessed chondritic material; a late veneer similar to that invoked for platinum groups elements (PGE) in the mantle. We note that the degree of depletion of volatile elements in the mantle resembles that of mantle PGE abundances, which are chondritic despite being highly depleted ($\sim$0.3% of PGE now in the mantle relative to chondritic abundances, e.g., Righter and Drake, 1997).

3 "Excess" noble gases in the atmosphere

In contrast, the atmosphere (for simplicity "atmosphere" is defined here as the combined atmosphere plus hydrosphere) displays clearly a different abundance pattern (Fig. 1: atmospheric volatile abundances are calculated as the mass of a given volatile element in the atmosphere divided by the mass of the Earth and normalized to the corresponding carbonaceous chondrite-like ratio). Water and nitrogen (N) have comparable abundances in the mantle and in the atmosphere, but noble gases in the atmosphere are enriched relative to the mantle abundances by at least one order of magnitude (for krypton the atmospheric enrichment factor is 24). It could be argued that the enrichment of noble gases relative to water and nitrogen in fact represents a deficit of the latter at the Earth's surface as a result of subduction and recycling into the mantle. However, the total atmosphere + mantle budget still shows a clear excess of Ne, Ar, Kr over water and N (Fig. 1). The "excess" of Neon could have been settled during the early evolution of the atmosphere. Indeed, Ne isotopic composition of atmospheric Ne; which is very different from that of mantle neon, is considered a result of isotopic fractionation of an initially solar-like gas during atmospheric escape (e.g., Dauphas, 2003; Pepin, 1991; Tolstikhin and Marty, 1998; Zanhle et al., 1988). In these models, atmospheric escape leaves a residual atmosphere rich in fractionated Ne. In contrast, these models do not predict atmospheric Ar and Kr excesses and further ad hoc processing is needed to account for the atmospheric pattern. We argue that these noble gases cannot be derived from the mantle, because they are not accompanied by the corresponding quantities of water and nitrogen at the surface of the Earth. They may instead originate from a contribution of material enriched in heavy noble gases relative to N and water. Icy planetesimals from the cold outer regions of the solar system, where even extremely volatile elements can be trapped cryogenically, are obvious candidates (Dauphas, 2003; Delsemme and Swings, 1952; Owen et al., 1992). Indeed, noble gas trapping-experiments with amorphous ice have reproduced the Ar-Kr-Xe pattern of both the Terrestrial and the Martian atmospheres (Notesco and Bar-Nun, 2005; Owen et al., 1992).

4 Kuiper belt – like cometary contribution to the atmosphere

Dynamical simulations indicate that the primary source of icy planetesimals for the LHB was beyond the present-day orbit of Neptune (Gomes et al., 2005). Such objects have an analogue in present day population of Kuiper-belt objects (KBOs), which formed and have been stored under very low ambient temperatures favourable to trapping of noble gases. There are several independent lines of evidence indicating that noble gases were efficiently trapped in icy planetesimals originating beyond 15 AU. First, despite the extremely low condensation temperatures of Helium and Neon ($\leq$20 K) (Bar-Nun et al., 1985; Lunine and Stevenson, 1985), these two elements have been recently detected in a cometary sample recovered by the Stardust spacecraft (McKeegan et al., 2006). Second, laboratory experiments with different mechanisms thought to be involved in cometary capture of noble gases, amorphous ice formation (Bar-Nun et al., 1985) or hydrous clathration (Delsemme and Swings, 1952; Iro et al., 2003; Lunine and Stevenson, 1985) have resulted in efficient trapping of heavy noble gases. Third, the abundances (relative to H) of C, N, S, Ar, Kr and Xe in the atmosphere of Jupiter are systematically enriched by a factors of 2–4 relative to the Sun, implying that these volatiles were delivered to Jupiter by objects formed at temperatures lower than about 30 K, i.e. originating in the Kuiper belt region (Owen et al., 1999). However, quantitative estimates of noble gas abundances in comets are not well constrained by direct spectroscopic observations (due to analytical difficulties) and published data have been questioned subsequently (see Bockelée-Morvan et al., 2004) for a review). Thus we derive our estimate of the noble gas content of the KBO-like bodies that contributed to the TLHB from laboratory experiments. Cryogenic noble gas capture is considered for the temperature range of 25–50 K. The lower temperature limit is consistent with temperatures deduced from the nuclear spin ortho/para-ratios observed for cometary H_2O and NH_3 and with the temperature-dependent fractionation of volatile

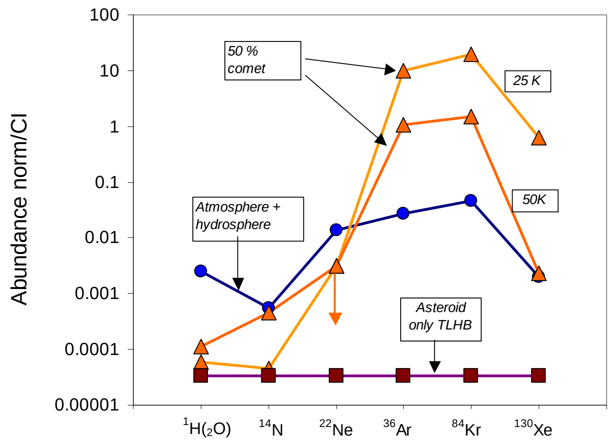

Fig. 2. The effect of the TLHB on the volatile abundances of the atmosphere (+ hydrosphere). Estimates of the mass contribution to Earth during the TLHB ranges from $\sim 1.8\times10^{23}$ g (based on dynamical modelling (Gomes et al., 2005)) to 2.2×10^{23} g (based on the lunar cratering record (Hartmann et al., 2000; Ryder et al., 2000), taking into account the surface ratio between the Earth and the Moon and a gravitational focusing factor of 3). For the calculations presented here, the average value (2×10^{23} g) is adopted. Atmospheric volatile abundances as a result of the TLHB are calculated for an even mixture of chondritic (i.e. asteroidal) and Kuiper-belt materials. Results are shown for two different formation temperatures for the Kuiper-belt material (25 K and 50 K, respectively). The calculated ^{22}Ne abundance represents an upper limit (Notesco and Bar-Nun, 2005). Note that a purely asteroidal TLHB (brown squares and lines at the bottom) would have had no discernable effect on the atmospheric composition.

elements trapped in amorphous ice compared to solar composition (Notesco and Bar-Nun, 2005). The upper temperature limit is chosen to conform to models of temperature evolution in the turbulent solar nebula, at distances $\geq$15 AU from the Sun (Hersant et al., 2001). Within this temperature range, abundances of captured heavy noble gases vary by one order of magnitude, and this variability is included in subsequent calculation. For a formation temperature of 50 K, the abundances of volatile elements are adopted from the compilation in Dauphas (2003). For a formation temperature of 25 K, experiments have shown (Notesco and Bar-Nun, 2005) that the total mass of trapped volatiles is about 10% of the mass of water ice, a result that is largely insensitive to the composition of the gas phase within rational limits. In order to compute N and Ar concentrations, a solar composition of the volatile element mass fraction is assumed for C, N and Ar. Elemental fractionation of noble gases relative to the solar composition (Notesco and Bar-Nun, 2005) was taken into account.

Figure 2 shows that a purely asteroidal (i.e. chondritic) TLHB would have left no observable imprint on the atmospheric composition. In contrast, an even mixture of KBOs and asteroidal materials during the TLHB in fact creates large over-abundance of Ar, Kr and Xe relative to the present day atmosphere, without affecting considerably the budget of major volatiles at the Earth's surface. It must be noted that, because laboratory experiments showed that, for the temperature range inferred for comet formation, Ne is not quantitatively trapped (Bar-Nun et al., 1985), and we do not expect atmospheric Ne to originate from the TLHB.

5 Implications for the mass contribution of icy planetesimals during the LHB

The process outlined in the previous section seems over-efficient. If one takes at face value the mass delivery of ET material during the TLHB (1.8×10^{23} g from modelling, 2×10^{23} g from extrapolation to Earth of the Lunar TLHB, 50% comets, 50% asteroids following Gomes et al., 2005), the amount of delivered Ar, Kr and Xe would exceed by 2–3 orders of magnitude the atmospheric budget for these elements (Fig. 2). To match the present day atmospheric noble gas abundances, either (i) the TLHB consisted of only $\sim$0.5% KBOs mixed in with a population of largely chondritic (i.e. asteroidal) impactors (Fig. 3), or (ii) cometary matter was less rich in noble gases than assumed in the present calculation, or (iii) noble gases were lost into space during the TLHB (atmospheric erosion, or preferential loss of volatiles from the impactor). Concerning (ii), the noble gas content of KBOs might have been depleted if cometary matter suffered heating subsequent to trapping of noble gases, for example during the transit of KBOs from their formation region to the inner solar system. With respect to (iii), we note that the amount of fissiogenic Xe from the decay of ^{244}Pu ($T_{1/2}$ = 82 Ma) in the atmosphere and the mantle is lower, but comparable to, the Xe isotope accumulation expected from close system accumulation; e.g., (Igarashi, 1986). Thus it seems unlikely that a 2 orders of magnitude atmospheric loss could have taken place at the time of the TLHB, when virtually all ^{244}Pu vanished, but it does not preclude the possibility of volatile loss from the impactors. Thus it is seems possible that the flux of KBOs to the inner Solar System during the TLHB was considerably less intense than proposed by Gomes et al. (2005).

6 Isotopic effects of the TLHB

Stable isotopes

In this section we estimate possible isotopic shifts of terrestrial volatiles due to the TLHB. The amounts of $H(_2O)$ and N carried by the TLHB were limited compared to both mantle and atmosphere inventories (Figs. 2, 3 and 4). Indeed the TLHB contribution that fits the atmospheric noble gas composition (Fig. 3) delivered 1.3 % and 6.0 % of atmospheric H_2O and N, respectively. The D/H ratios of cometary H_2O (3×10^{-4}) (Bockelée-Morvan et al., 2004) is higher than the terrestrial value (1.5×10^{-4}) by ∼1000‰, so that the TLHB might have shifted the ocean D/H ratio by a few ‰. The shift would have been lower if the atmosphere and the mantle exchanged water significantly during Earth's history. The few available measurements of N isotopic ratios of comets suggest that the N isotopic composition of cometary matter is highly un-equilibrated, with δ^{15}N values ranging from −160‰ in HCN (Jewitt et al., 1997) to +800‰ in CN (Arpigny et al., 2003). Taken at face value, these data suggest that a contribution of 6 % cometary N might have induced a significant shift of terrestrial δ^{15}N, within −10‰–+50%, clearly significant since most Terrestrial δ^{15}N variations span over 20‰ only. The actual effect might have been more limited due to averaging of the different cometary N components, but this point is for the moment impossible to investigate due to the lack of relevant data. No shift is expected for the carbon isotopic composition in the light of presently available data for comets which indicate a "normal" C isotope composition (Jewitt et al., 1997).

Noble gases

In our view, atmospheric Ne predated the TLHB and its isotopic composition was settled by earlier processes. The Ar and Kr isotopic compositions of potential Solar System reservoirs (Sun, Phase "Q") are close to the atmospheric values, and limited isotopic fractionation of original noble gases, either during cometary formation and processing, or during atmospheric processing on the Earth before the LHB, can account for the slight isotopic differences between the atmosphere and potential end-members (Dauphas, 2003). It is not clear if atmospheric Xe was effectively delivered by comets during the TLHB, or if Xe contribution from comets was insignificant due to Xe depletion in cometary matter (Bar-Nun et al., 1985; Owen et al., 1992). for the first possibility, a test will be the analysis of the isotopic composition of Xenon in cometary matter. This precise measurement will require to have cometary matter in the laboratory in excess of the tiny quantity returned by Stardust, and will await for a future cometary sample return mission dedicated to return "large" samples of a comet. The second case has been modelled by Dauphas (2003).

7 Comparison with the long term background flux of ET matter to Earth

Other sources of ET matter on Earth need to be evaluated as potential suppliers of noble gases to the atmosphere before assigning a prominent role for the TLHB. The long-term ET flux onto the Earth's surface comprises two main components. A continuous flux of 20 000–40 000 tons/yr (e.g., Love and Brownlee, 1993) of small particles (IDPs, micrometeorites) represents by far the main continuous flux of ET matter on Earth, as the mass ratio between IDP and meteorites is 10^2–10^3 (Bland et al., 1996). This flux might have not varied dramatically since 3.8 Gyr ago, except for a possible increase in the last 0.5 Gyr, recorded in lunar soils (Culler et al., 2000; Hashizume et al., 2002). A near-constant, within a factor of ∼2, ET contribution to the inner solar system since 3.8 Gyr ago is consistent with the cratering record at the lunar surface (Hartmann et al., 2000), assuming that large objects and dust are linked. The mass contribution due to large objects might have been comparable to the IDP flux over the last 3 Gyr (Anders, 1989; Kyte and Wasson, 1986; Trull, 1994).

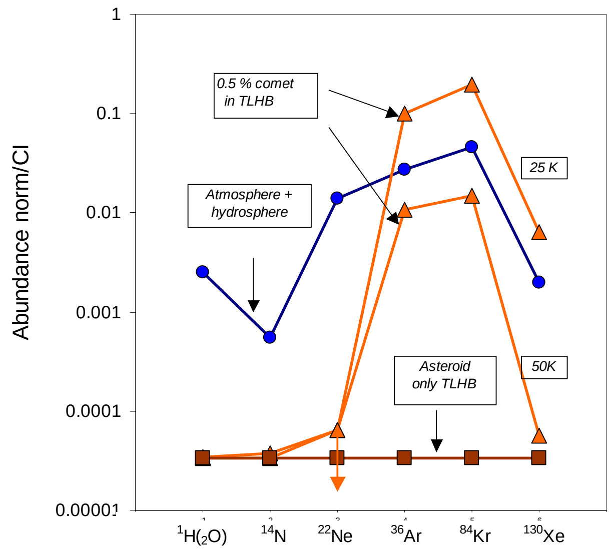

Fig. 3. Same as Fig. 2 but for a Kuiper-belt mass fraction of 0.5% in the cometary/asteroidal mix.

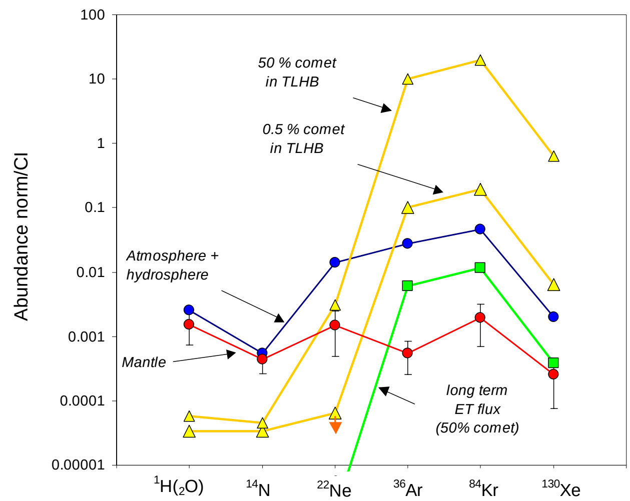

Fig. 4. Comparison of the delivery of volatile elements by the long-term flux of ET matter assumed to be made of 50% cometary matter mixed with 50% asteroidal matter (green symbols and lines) with delivery of the same elements by the TLHB (yellow symbols and lines). The trapping temperature for cometary matter is 25 K in all cases.

The total mass of ET matter delivered to Earth since 3.8 Gyr ago was $\sim 2\times 10^{20}$ g, which is 3 orders of magnitude lower than the mass delivered during the TLHB ($\sim 2\times 10^{23}$ g). A conservative estimate of the impact of the long term flux on the noble gas budget of the atmosphere can be made by assuming that this flux consisted of 50% cometary matter, and that the latter did not loose its noble gas load since their trapping at a low temperature of 25 K. This assumption will lead to an upper limit because heating of small particles by the Solar radiation during the transit to the inner solar system will inevitably decrease the noble gas content of small particles. Under these assumptions, the maximum noble gas contribution due to the long term delivery of ET material to Earth is lower than the noble gas amount added by the TLHB (Fig. 4), which also fails to account for the present-day noble gas content of the atmosphere. However, given the uncertainties involved in this computation (probably one order of magnitude), we cannot exclude a significant contribution of cometary noble gases to the Earth's atmosphere by the long-term ET flux. Arguments given above nevertheless suggest that its contribution was minor relative to the one linked with the TLHB.

8 Conclusions

The atmospheric noble gas excess appears to be a direct signature of the TLHB, provided that the material delivered to the surface of the Earth comprised some material originating from the Kuiper-belt (Gomes et al., 2005). The fraction of cometary matter in the TLHB necessary to account for the noble gas inventory of the atmosphere ($<1\%$) is much lower than the one predicted by modelling ($\sim 50\%$, Gomes et al., 2005). Among possible causes of this discrepancy, modelling parameters or degassing of cometary material en route to the inner Solar system must be considered. Considerable amounts of organics of variable complexity would have been co-delivered during the TLHB (Anders, 1989). From noble gas excesses in air, it is estimated (based on the abundances of volatile compounds in comets, Bockelée-Morvan et al., 2004) that $1–5\times 10^{19}$ g of organic C was added to Earth by the TLHB, which is comparable to the mass of the present-day biosphere (1.15×10^{19} g). The TLHB might have also provided the energy and created the redox conditions necessary to synthesize complex organics.

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