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eEarth Discussions

Interactive comment on "Noble gas signature of the late heavy bombardment in the Earth's atmosphere" *by* B. Marty and A. Meibom

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Response to Comments by reviewers

B. Marty and A. Meibom

We are grateful to both reviewers for their constructive reviews which helped us a lot to prepare a revision. Below we answers their concerns and comments point by point. The most important changes we did was to address in a specific new section and in a new Figure (Fig. 4) the strength of other ET sources relative to the TLHB, and to detail more, also in a new section, the consequences of the TLHB on the isotopic ratios of atmophile elements

Response to comments by Reviewer #1 (Rainer Wieler)

We thank the reviewer for allowing us to discuss more the flux of volatile elements onto the Earth's surface. The reviewer raises an important point that was not explored in our contribution and that certainly deserves attention. The long-term flux of extraterrestrial material reaching the Earth might have been partly made of cometary material, and previous attempts to estimate the delivery flux of volatile elements should be revised accordingly. Below we answer reviewers' comments following the same numbers given in his review.

Nr. 1 : We agree that we have to compare the TLHB delivery with the contribution of long-term extraterrestrial (ET) material to the Earth's surface. A direct comparison using mass fluxes is not adequate because the time interval of the TLHB is under-constrained. We prefer to compare the integrated masses delivered by each source instead. The long-term ET flux onto the Earth's surface comprises schematically two 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 major source of ET delivery by small objects. This flux, thereafter labelled the IDP flux, might have not varied dramatically since 3.8 Gyr ago, except for a possible increase in the last 0.5 Gyr, as recorded in lunar soils (Culler et al., 2000; Hashizume et al., 2002). A near-constant, within a factor of $\sim$2, ET contribution to the inner solar system since 3.8 Gyr ago is also consistent with the cratering record at the lunar surface (Hartmann et al., 2000). 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). The total mass delivery of ET matter to Earth since 3.8 Gyr ago is $\sim$2 x 10^{20} g, which is 3 orders of magnitude lower than the mass delivered during the TLHB. 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 consists in 50 % cometary matter, and that the latter did not lost its noble gas load since trapping at a low temperature of 25 K. The latter may not be true due to heating of small particles by the Sun during the transit to the inner solar system. Under these assumptions, one obtains a maximum noble gas contribution comparable to, but lower than the noble gas amount added by the TLHB (Fig. 4). It also fails to account for the present-day noble gas content of

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the atmosphere, but may be significant compared to the mantle noble gas budget. However, given the uncertainties involved in this computation (probably one order of magnitude), we cannot exclude a sizeable contribution of cometary noble gases to the Earth's atmosphere by the long-term ET flux. Arguments given above suggest that its contribution was minor relative to the one linked with the TLHB, provided of course that the latter was partly made of Kuiper belt-like objects.

Nr. 2: The typo error has been corrected. The N-^{40}Ar-^{36}Ar relationship among terrestrial reservoirs and their bearing on the cycle of nitrogen between the mantle and the surface of the Earth are fully discussed by Marty and Dauphas (2003).

Nr.3: First it should be noted again that normalization to CI does not imply that mantle volatiles are chondritic in origin. We estimated the mantle concentration of each volatile element, and divided it by the concentration of the same element in Orgueil. The fact that, doing so, one obtains a flat, roughly chondritic-like pattern is the outcome of this approach and not its starting assumption. Whether or not this has implication for the origin of mantle volatiles is not the focus of this contribution, but is discussed in Marty and Yokochi (2006). The reviewer is surprised that, given the high degree of degassing of the mantle, volatiles appear little fractionated relative to CI. Our point is that depletion does not necessarily implies fractionation, for example, the low noble gas content of the mantle could be due to mixing a minute amount of volatile-rich material with a completely dry mantle material. We briefly mention this point in the revised version.

Nr.4: OK we have changed the text accordingly. All noble gases are enriched in the atmosphere relative to the mantle.

Nr. 5: We acknowledge that remote measurements of Ar in comets have led to contrasted conclusion, precluding to derive estimates of the noble gas content in comets from these attempts. We rewrote the sentence. This re-enforces the use of laboratory data to estimate the noble gas content of comets.

Nr.6: The reviewer requests clarification concerning the role of the TLHB for settling the "Ne excess" of the atmosphere. We argue that this possibility is not consistent with laboratory experiments which show that, for the temperature range inferred for comet formation, Ne is not well trapped. Thus atmospheric neon needs to have been settled in the Hadean before the TLHB. There exist a wide literature concerning elemental and isotopic fractionation of Non during the early evolution of the atmosphere. For instance, a model of mantle-atmosphere evolution in which cometary matter is added lately has been fully developed by Dauphas, 2003). This author showed that this mixed origin of the atmosphere and the oceans give results fully accounting for both elemental abundances and isotopic ratios of noble gases in the mantle and in the atmosphere. In this contribution, we do not aim to repeat this work and instead evaluate the effect of the TLHB under the conclusion of Gomes et al. (2005) that it consisted partly of Kuiper belt objects. As for Xe, it is not clear of atmospheric Xe was effectively contributed by comets, or if Xe contribution from comets was insignificant due to Xe depletion in cometary matter as suggested by laboratory experiments. We have clarified this point in the text.

Nr.7: a : Please refer to our answer to Nr.1: it seems that the long-term ET flux cannot fully account for the atmospheric noble gas content, whereas the TLHB is extremely efficient for supplying noble gases to the terrestrial atmosphere. b : We already have cautioned the reader that an apparent 0.5 % cometary contribution in the TLHB could also be the result of a lower noble gas contents in comets than ,the one we inferred, due to degassing of cometary matter en route to the inner solar system. Other possibilities exist like atmospheric loss during impact, but such a late loss is not consistent with the Xe isotopic composition of the atmosphere indicating atmospheric closure some 100-200 Myr after solar system condensation, e.g., Pepin (2006) and refs therein. Conversely, volatile elements from the impactors might have been lost to space during shocks.

Response to comments by Reviewer #2 (Manuel Moreira)

We are pleased to read that the reviewer finds our approach interesting. We hope that the crime of lese majesty will not end up on the Guillotine for us and have added reference to the Paris group's work. We address the three points that the reviewer has raised in the same order.

Normalisation to CI

A priori, the normalisation to CI is no intended to infer that mantle volatiles are derived from a CI-like source. This normalisation is used because it gives a convenient format for comparing reservoirs with enormous variations of their noble gas concentrations, and illustrates clearly the extreme depletion of noble gases in asteroidal matter compared to the protosolar nebula (PSN) composition . It happens that the normalisation leads to a roughly flat (CI) pattern for the mantle reservoir and this has certainly implication for sources and processes of terrestrial volatiles, and some of these are discussed in Marty and Yokochi (2006). Normalising to another type of chondrites would not change the underlying message of our approach : noble gases are highly depleted in asteroidal material relative to H_2O, (C), N, halogens and other volatile species, compared to the PSN composition or any reservoir derived from the PSN by condensation at very low temperature. The reviewer proposes to use instead a normalisation to a E-chondrite composition, in order to avoid a second crime of lese majesty. For N and noble gases, this would not make any change (N and noble gases are trapped in organic phases, not necessarily the same ones, but which proportions relative to silicates and metal vary conjointly). It must be noted that our conclusion that a cometary TLHB is unable to account for the budget of water on Earth is even firmer in the case of a E-chondrite normalisation.

Isotopic ratios

Reviewer # requires more detail about consequences of the TLHB on H, N, noble gas isotopic ratios. The amounts of H($_2$O) and N carried by the TLHB are very small com-

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pared to both mantle and atmosphere+oceans inventories (Figs. 2, 3 and 4). The TLHB delivery that fits the atmospheric noble gas composition (0.5 % comet, Fig. 3) will contribute only 1.3 % (H_2O) and 6.0 % (N). The D/H ratios of cometary H_2O around 3 x 10^{-4} (Bockelée-Morvan et al., 2004) is higher than the terrestrial value (1.5 x 10^{-4}) by ~1000 8240;, so that the TLHB might have shifted the ocean D/H ratio by a few 8240;. Whether or not such a shift can be recognized in old and generally highly metamorphosed sediments contemporary to the TLHB will require further detailed study. The few available measurements of N isotopic ratios of comets suggest that the nitrogen isotopic composition of cometary matter is highly unequilibrated, with δ^{15}N values from - 160 8240; in HCN (Jewitt et al., 1997) up to +800 8240; in CN (Arpigny et al., 2003). Taken at face value, these ratios suggest that a contribution of 6 % cometary N might have induced a significant shift from -10 8240; up to +50 %, although the real isotopic shift might have been less pronounced due to isotope homogenisation of cometary N during the shock event. Further insight into N isotopic effects will requires better knowledge of the isotopic composition of nitrogen in comets.

For noble gases, much as been said by (Dauphas, 2003) in detail and will not be repeated here. In our view as well as in the view of Dauphas (2003), most Kr and Ar are from comets. The Ar and Kr isotopic compositions of potential ET reservoirs (Solar, phase Q) are close to the atmospheric one, 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. For neon, laboratory experiments predict very little, if any (Bar-Nun and Owen, 1998), trapping during ice formation event at 25 K, which implies that the neon inventory of the atmosphere was settled before the TLHB (Dauphas, 2003). Its isotopic composition was possibly established previously during atmospheric escape by isotope fractionation of an initially solar Ne isotope composition , as classically proposed since two decades (e.g., Pepin, 1991). However, recent analysis of Stardust cometary matter suggests another direction. Two laboratories (CRPG Nancy, France, and Univ. Minnesota, Minneapolis, USA) have found Ne with an isotopic composition undistinguishable from Ne-Q, and closer to the Ne atmospheric composition than that of Solar Ne. Furthermore the Ne abundance in the analysed sample was much higher than in chondritic material and could account well for the Ne atmospheric inventory when the TLHB flux is used. We do not mean that a single grain analysis will solve definitely the problem, but wish to point out a better insight into cometary composition before we are in a position to decide between the above alternatives. We do not mention this point in the revised ms. because these data are in a ms. under review.

Contrary to Ar and Kr, the Xe isotopic composition differs by 2-3 % per amu from both Solar and Phase Q (asteroidal) isotopic compositions. In order to account for this difference, one can postulate that cometary Xe is isotopically fractionated to this extent, but testing this will require a direct analysis of cometary Xe. Alternatively, Xe could be depleted in comets (Dauphas, 2003), as suggested from laboratory experiments which shows that Xe is less efficiently trapped in growing ice than Kr and Ar (Owen et al., 1992). In this case, the TLHB contribution to atmospheric Xe was limited (Fig. 3) and the Xe isotopic composition of the atmosphere was mainly settled before the TLHB, following processes like the ones described in the literature (e.g., (Pepin, 1991; Sasaki and Nakasawa, 1988; Tolstikhin and Marty, 1998). For the moment, it is not possible at this stage to decipher between these possibilities.

Water contribution

The reviewer is correct : about 1 % of oceanic water could have been contributed by Kuiper belt objects during the TLHB, see above for potential isotopic effects.

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Detail of changes done in the ms.

Rev. #1

Page and line numbers refer to the annoted copy supplied by Rainer Wieler

Abstract : we have tuned down our assertion concerning the role of the TLHB. We have been less specific about the exact fraction of KPO in the TLHB, noting that it represents < 1 %.

Page 100, Line 18 : We have added a section by the end of the ms where we compare the impact of the TLHB with that of the long term flux of ET matter on Earth.

Page 101, Line 23 : We replaced "Here we show that..." by "In this contribution, we suggest that..."

Page 102, Line 15 : Reference to on-line material removed

Page 103, Line 2 : we do not wish to change the text with reference to Nr. 2 comment. We think that the present text is explicit enough : "The nitrogen content was estimated from ^{40}K-^{40}Ar-N systematics of mantle-derived rocks (Marty, 1995; Marty and Dauphas, 2003)."

Page 103, line 14 : typo corrected.

Page 104, line 5 : We added a few sentences to take into account the remark by the reviewer concerning the apparent lack of elemental fractionation of mantle volatiles despite their severe depletion. We note indeed that no fractionation is expected in the case of mixing of a totally degassed mantle with tiny patches of unprocessed material and make a parallel with the case of PGE.

Page 104, line 12 : "Heavy noble gases" replaced by "noble gases". Ne is included as an excess; However, it is not evident that Xe is also in excess compared to water or nitrogen in the surface reservoir. The Xe/N ort Xe/H_2O ratios of the atmo-

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sphere+hydrosphere and the mantle are indeed comparable. We have added a sentence to be more specific about the origin of atmospheric neon.

Page 105, line 23 : we acknowledge that there is no reliable data for the noble gas composition of comets.

Page 106, line 7 : Ref. to comet variability removed.

Page 106, line 24 : We have tuned down our assertion that the TLHB should have contained 0.5 % cometary matter. We suggest alternative ways to fit the atmospheric inventory, like atmospheric erosion (but in this case we note that Xe isotopes did not record this event), or cometary matter degassing.

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Crime of lese Majesty repeared, ref. to Staudacher and Allègre (1982) and Kunz et al. (1998) added.

Isotopic effects developed in a new section

Page 101, line 29 : Now "Xenon (Xe) isotope systematics indicate extensive mantle degassing..."

Page 103, line 6 : 20 km3/yr changed

Page 103, line 18 : The origin of the 22Ne content is now better explained : "With the ^{22}Ne content of the bulk mantle of 4.0 x 10^{-15} mol/g estimated from N-Ar systematics and noble gas patterns of the mantle with the method outlined above,..."

Page 104, line 4 : the dilution possibility is now discussed in the text

Page 104, line 10 : No assumption on the degassing state of the Earth is made. We just normalize a volatile reservoir to a solid (the Earth) for the purpose of comparison.

Page 104, line 17 (the possibility that the apparent under-abundance of water and N relative to noble gases is due to preferential loss of water and N) : First, the atmospheric pattern does not resemble to a fractionated mantle-like (CI), and a solar composition would contain too little N and watert to start with. Second, the D/H ratio of the oceans is within that of chondrites. This coincidence could be fortuitous, but the excellent match between these reservoirs suggests a genetic relationship and no room for isotope fractionation that would have accompanied atmospheric loss.

There are no units on the y-axis of figures. The numbers are dimensionless ratios.

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