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## Origins of volatile elements (H, C, N, noble gases) on Earth and Mars in light of recent results from the ROSETTA cometary mission

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1       Origins of volatile elements (H, C, N, noble gases) on Earth and Mars in light of  
2               recent results from the ROSETTA cometary mission

3  
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## 24 **Abstract**

25 Recent measurements of the volatile composition of the coma of Comet 67P/Churyumov-  
26 Gerasimenko (hereafter 67P) allow constraints to be set on the origin of volatile elements (water,  
27 carbon, nitrogen, noble gases) in inner planets' atmospheres. Analyses by the ROSINA mass  
28 spectrometry system onboard the Rosetta spacecraft indicate that 67P ice has a D/H ratio three times  
29 that of the ocean value (Altwegg et al., 2015) and contains significant amounts of N<sub>2</sub>, CO, CO<sub>2</sub>, and  
30 importantly, argon (Balsiger et al., 2015). Here we establish a model of cometary composition based  
31 on literature data and the ROSINA measurements. From mass balance calculations, and provided  
32 that 67P is representative of the cometary ice reservoir, we conclude that the contribution of  
33 cometary volatiles to the Earth's inventory was minor for water ( $\leq 1\%$ ), carbon ( $\leq 1\%$ ), and nitrogen  
34 species (a few % at most). However, cometary contributions to the terrestrial atmosphere may have  
35 been significant for the noble gases. They could have taken place towards the end of the main  
36 building stages of the Earth, after the Moon-forming impact and during either a late veneer episode  
37 or, more probably, the Terrestrial Late Heavy Bombardment around 4.0-3.8 billion years (Ga) ago.  
38 Contributions from the outer solar system via cometary bodies could account for the dichotomy of  
39 the noble gas isotope compositions, in particular xenon, between the mantle and the atmosphere. A  
40 mass balance based on <sup>36</sup>Ar and organics suggests that the amount of prebiotic material delivered by  
41 comets could have been quite considerable – equivalent to the present-day mass of the biosphere. On  
42 Mars, several of the isotopic signatures of surface volatiles (notably the high D/H ratios) are clearly  
43 indicative of atmospheric escape processes. Nevertheless, we suggest that cometary contributions  
44 after the major atmospheric escape events, e.g., during a Martian Late Heavy Bombardment towards  
45 the end of the Noachian era, could account for the Martian elemental C/N/<sup>36</sup>Ar ratios, solar-like  
46 krypton isotope composition and high <sup>15</sup>N/<sup>14</sup>N ratios. Taken together, these observations are  
47 consistent with the volatiles of Earth and Mars being trapped initially from the nebular gas and local  
48 accreting material, then progressively added to by contributions from wet bodies from increasing  
49 heliocentric distances. Overall, no unified scenario can account for all of the characteristics of the

50 inner planet atmospheres. Advances in this domain will require precise analysis of the elemental and  
51 isotopic compositions of comets and therefore await a cometary sample return mission.

## 52 **1. Introduction**

53  
54 According to cosmochemical constraints and simulations, the inner planets grew first "dry", and  
55 water and atmophile elements were contributed later on by volatile-rich objects originating from  
56 larger heliocentric distances (Morbidelli et al., 2000; Raymond et al., 2004; Albarède et al., 2013;  
57 Marty, 2012). A cometary origin for the Terrestrial oceans, the atmosphere and the organics is often  
58 advocated (Oro, 1961; Anders and Owen, 1977; Safronov, 1972) because (i) comets are volatile-rich  
59 as they contain abundant organics and ices (30-50 wt. % H<sub>2</sub>O), and (ii) their high eccentricities and  
60 hyperbolic trajectories increase their probability to encounter inner solar system bodies. Other  
61 potential sources of water are "wet" asteroids. Meteorites are generally dry, although some of them,  
62 the carbonaceous chondrite clan, can contain up to 15 wt. % equivalent H<sub>2</sub>O as hydrated phases.  
63 Because these phases are remnant of water-rock interactions on asteroids, the original water content  
64 could have been significantly higher, possibly matching those of comets. This would argue in favor  
65 of a continuum between meteoritic and cometary compositions in the past. The Terrestrial oceans  
66 ( $1.5 \times 10^{24}$  g) correspond to 0.025 % of the Earth's mass. Taking into account water in the deep Earth  
67 may raise the Terrestrial H<sub>2</sub>O inventory to a maximum of 0.2 wt. % (Marty, 2012). Assuming  
68 conservation of volatile elements during impacts, that is, no loss of volatiles to space (an assumption  
69 discussed later on), Terrestrial water could have been supplied by a few wt. per mil to a few wt.  
70 percent of cometary, or asteroidal, material to a dry proto-Earth, leaving the bulk chemical  
71 composition of Earth little affected.

72 Dynamical models suggest that, during its formation, the Earth accreted water and other volatile  
73 elements predominantly from planetesimals parented to primitive asteroids, i.e. with composition  
74 similar to carbonaceous chondrites (Morbidelli et al., 2000; Raymond et al. 2004, 2007; O'Brien et  
75 al., 2006, 2014). Comets, intended as planetesimals of trans-Neptunian origin, should have had a  
76 negligible contribution during Earth's accretion. Instead, once the Earth's formation was completed,

77 possibly several hundreds of million years (Ma) afterwards, the Earth should have accreted non-  
78 negligible amounts of mass from asteroids and/or from icy bodies of trans-Neptunian origin, during a  
79 dynamical instability event that re-structured the orbital configuration of the giant planets (the so-  
80 called "Nice model"; Gomes et al., 2005). These models predict contributions of icy bodies in  
81 proportions comparable to those of asteroids. From the lunar impact crater record, Chyba (1990)  
82 argued that the Earth could have acquired an exogenous ocean around 4 Ga ago if comets comprised  
83  $\geq 10$  wt. % of the impacting population. Marty and Meibom (2007) made the point that, if comets  
84 contain noble gases in amount predicted by laboratory ice trapping experiments (see below), then the  
85 fraction of cometary material in the late heavy bombardment on Earth could not have been more than  
86 0.5 %, as constrained by the noble gas inventory of the atmosphere.

87 Cometary contributions might have left an imprint in the composition of the ocean-atmosphere.  
88 Owen and Bar-Nun (1995) noted that the noble gas elemental composition of the atmospheres of  
89 Mars and Earth (which are different from those of chondrites by having a one order of magnitude  
90 lower Xe/Kr ratio, Fig. 1), are consistent with a cometary origin. Experiments of noble gas trapping  
91 in growing amorphous ice have shown that the absolute amounts and their relative proportions  
92 depend on the trapping kinetics, pressure and, importantly, temperature (Bar-Nun et al., 1985). Owen  
93 and Bar-Nun (1995) proposed a cometary ice formation temperature of 50 K to account for the  
94 Martian and Terrestrial Ar/Kr/Xe ratios. Other works questioned the relevance of these experimental  
95 conditions to those of the protosolar nebula (Notesco and Bar-Nun, 2005; Yokochi et al., 2012) or  
96 preferred trapping of cometary noble gases in clathrates rather than in amorphous ice (Mousis et al.,  
97 2010). Importantly, because Xe from the protosolar nebula is expected to be quantitatively trapped in  
98 cometary ice (Notesco and Bar-Nun, 2005; Yokochi et al., 2012; Mousis et al., 2010) and because  
99 physical adsorption does not induce significant Xe isotope fractionation (Marrocchi and Marty,  
100 2013), cometary Xe should have a solar-like isotopic composition. However, the xenon isotopic  
101 compositions of the atmospheres of Earth and Mars are not solar (nor chondritic), being enriched in  
102 the heavy isotopes relative to the light ones by 3-4 % per atomic mass unit (Fig. 1). Taking into

103 account this discrepancy, Dauphas (2003) proposed a dual origin for the Terrestrial atmosphere. In  
104 his model, a primary atmosphere of solar composition was lost to space, leaving residual gases  
105 mostly made of isotopically fractionated Xe. Then comet-like bodies contributed noble gases  
106 depleted in Xe (following the same argument as Owen and Bar-Nun, 1995, that cometary ice should  
107 depleted in Xe compared to Chondritic and other noble gases, Fig. 1). This model accounts  
108 successfully for the elemental and isotopic compositions of atmospheric noble gases and for the  
109 "xenon paradox": Atmospheric xenon is depleted relative to Chondritic Xe but also relative to  
110 atmospheric Kr, and enriched in its heavy isotopes relative to any known cosmochemical  
111 composition (Fig. 1), both properties being paradoxical if xenon depletion was due atmospheric  
112 escape. However, the Xe paradox might be related to a different process and may not be a diagnostic  
113 of source composition. Indeed, from the analysis of ancient (>2.7 Ga-old) minerals, Pujol et al.  
114 (2011) argued for continuous loss and isotopic fractionation of atmospheric xenon to space through  
115 geological time as a cause of the peculiar composition of atmospheric Xe. Therefore the xenon  
116 paradox might be due to secondary long-term processing and not to a source effect.

117 The hydrogen and nitrogen isotopes give independent insight into the origin(s) of planetary  
118 volatiles (e.g. Alexander et al., 2012; Marty, 2012; Füri and Marty, 2015; Fig. 2). Taken together,  
119 they suggest an asteroidal, rather than cometary, origin for nitrogen and water in the Terrestrial  
120 atmosphere and the oceans. The D/H ratios of comets are generally higher by a factor of 2-3 relative  
121 to the ocean's value and to most of the chondritic values, prohibiting a genetic relationship between  
122 cometary ice and Terrestrial water. Available data are mostly from long-period comets thought to  
123 originate from the Oort cloud. The measurement of an ocean-like D/H ratio for a Jupiter family  
124 comet (Hartogh et al., 2011), presumably originating from the Kuiper belt, suggests a D/H  
125 heterogeneity among comet families. Recently, a D/H value three times the ocean's has been  
126 measured in the coma from Comet 67P/Churyumov-Gerasimenko (thereafter 67P), also a Jupiter  
127 family member (Altwegg et al., 2015). The nitrogen isotopes give a similar story. Chondrites have  
128 variable N isotope ratios which distribution coincides with the Terrestrial composition. In contrast,

129 comets have  $^{15}\text{N}/^{14}\text{N}$  ratios about two times the Terrestrial and bulk chondritic values (Fig. 2). One  
130 possible caveat is that only HCN, CN, and  $\text{NH}_2^+$  could be measured at distance by spectroscopy  
131 (there is no in-situ measurement on a comet), and it is not clear if these nitrogen species are  
132 representative of bulk cometary N.

133 In this contribution we use the recent compositional data of the 67P coma obtained by the  
134 ROSINA mass spectrometer on board of the ROSETTA spacecraft to set constraints on the origin(s)  
135 of volatile elements on Earth and Mars. Importantly, this instrument measured for the first time a  
136 noble gas - argon - in cometary gases (Balsiger et al., 2015). We present first a model composition  
137 for cometary matter using literature data and assuming that 67P is representative of the cometary  
138 reservoir. We then attempt a mass balance to infer the possible contribution of the outer solar system  
139 to the Terrestrial and Martian inventory of water, carbon, nitrogen and noble gases.

## 140 **2. Reservoir inventories**

### 141 *2.1. Comets*

#### 142 *2.1.1. Elemental abundances*

143 The chemical and isotopic compositions of comets is constrained by (i) in-situ measurements by  
144 spacecrafts (e.g., A'Hearn et al., 2011; Le Roy et al., 2015; Jessberger et al., 1988; Kissel and  
145 Krueger, 1987) (ii) spectroscopic observations of comae (e.g., Bockelée-Morvan, 2011; Mumma and  
146 Charnley, 2011), and (iii) laboratory analysis of cometary grains recovered by the Stardust mission  
147 (Brownlee, 2006) and of interplanetary dust particles presumably of cometary in origin (e.g., Duprat  
148 et al., 2010).

149 Comets are made of refractory silicates and metal, refractory and non-refractory organics, and ices  
150 (Jessberger et al., 1988; ; Kissel and Krueger, 1987; Mumma and Charnley, 2011; Bockelée-Morvan,  
151 2011). The analysis of cometary grains recovered by the Stardust mission revealed the occurrence of

152 several high temperature phases reminiscent of chondritic material. These are calcium-aluminium  
153 rich inclusions, chondrules and refractory olivines. Stable isotope compositions of these phases  
154 indicate an inner solar system origin for this material (Brownlee, 2006). From mass balance, silicate  
155 + metal (Si, Mg, Fe) grains make about 25-30 wt. % (Jessberger et al., 1988). Refractory organics  
156 constitute a significant fraction of C and, to a lesser extent, of N and H, and must be taken into  
157 account in the bulk composition of cometary matter (Greenberg, 1998). This is confirmed by a  
158 refractory organics/silicate+metal ratio close to 1 for dust emitted by comet Halley (Kissel and  
159 Krueger, 1987). Therefore, organic refractory particles (the so-called CHON grains, Jessberger et al.,  
160 1988) could make another 25-30 wt. %, and non-refractory carbon-bearing species could contribute  
161 about 4-8 wt. % (Greenberg, 1998). The proportion of ice amounts for 30-50 wt. %. The composition  
162 of comae (Table 1) gives insight into the ice composition ( $\sim 80$  wt. %  $\text{H}_2\text{O}$  with  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_3\text{OH}$ ,  
163  $\text{CH}_4$ ,  $\text{H}_2\text{S}$ , and N-compounds including  $\text{CN}$ ,  $\text{HCN}$ ,  $\text{NH}_3$  and  $\text{N}$ ; Bockelée-Morvan, 2011; Hässig et  
164 al., 2015; Rubin et al., 2015).

165 Noble gases are able to set stringent constraints on the origin of planetary volatiles on one hand,  
166 and on processes and conditions of comet formation on another hand. Unfortunately the abundances  
167 of noble gases in comets are essentially unknown as these elements are extremely difficult to detect  
168 by spectroscopy. Stern et al. (2000) proposed an Ar/O ratio of  $1.8 \pm 1.0 \times 10^{-4}$  for Comet Hale Bopp,  
169 lower than the solar value of  $46 \times 10^{-4}$  (Weaver et al., 2002, and refs. therein), but this estimate has  
170 not been confirmed. Weaver et al. (2002) suggested that the cometary Ar/O ratios are lower than  $42 \times$   
171  $10^{-4}$ , based on three comet observations. The only reliable set of measurements are those done on 67P  
172 coma using the ROSINA mass spectrometer which directly the 67P coma composition (Balsiger et  
173 al., 2015). They indicate a  $^{36}\text{Ar}/\text{H}_2\text{O}$  varying between  $0.1 \times 10^{-5}$  and  $2.3 \times 10^{-5}$  during the 3 days  
174 measurement period. Considering that  $\text{Ar}/\text{O} \sim 1.3 \text{ Ar}/\text{H}_2\text{O}$  (Weaver et al., 2002), and taking into  
175 account a solar isotope composition for argon ( $^{40}\text{Ar} \sim 0$ ,  $^{38}\text{Ar}/^{36}\text{Ar} = 0.183$ ), the corresponding Ar/O  
176 range of 67P is  $0.01\text{-}0.35 \times 10^{-4}$ , thus lower than the upper limits given above, and 2-3 orders of  
177 magnitude lower than the solar ratio of  $46 \times 10^{-4}$ . It is worth mentioning that even if noble gases are



178 mostly hosted in ices, refractory grains may also contain large amounts of these elements, as  
179 suggested by the discovery of high He and Ne abundances in grains of comet Wild2 recovered by the  
180 Stardust spacecraft (Marty et al., 2008). However, a mass balance is not possible due to the lack of  
181 relevant Ar data, and we adopt here the 67P coma composition.

### 182 *2.1.2. Isotopes*

183 The stable isotope ratios relevant to this study are the D/H ratios of comets, with special reference  
184 to the 67P value ( $[5.3 \pm 0.7] \times 10^{-4}$ ,  $\sim 3$  times the ocean water ratio; Altwegg et al., 2015), and N  
185 isotope variations depicted in Fig. 2, although no data are yet available for 67P. For noble gases,  
186 only the  $^{36}\text{Ar}/^{38}\text{Ar}$  ratio has been measured in the coma of 67P ( $5.4 \pm 1.6$ ; Balsiger et al., 2015),  
187 consistent with a solar system composition, but with a precision too low to permit identification of a  
188 specific cosmochemical component. Models of ice formation from a protosolar nebula gas predict  
189 that the isotopic composition of noble gases are solar. However, there is considerable uncertainty  
190 arises for the mode of trapping (i.e., neutral versus ionized) which may fractionate, or not, noble gas  
191 isotopes, and for the local composition of the gas during ice formation. Furthermore, the analysis of  
192 Stardust refractory grains revealed a high abundance of light noble gases and has shown that the  
193 neon isotope composition is closer to a meteoritic signature than to a solar one, precluding to  
194 establish a definite composition for cometary noble gases. Measurements of noble gas isotopes in  
195 comets should be given a high priority in future space programmes. In the absence of such, we only  
196 discuss here the case of argon. The model cometary composition is given in Table 2. The  
197 uncertainties represent the range of values observed in comets, unless a single set of values is  
198 available.

### 199 *2.2 Carbonaceous chondrites*

200 For noble gases, we use a literature survey of 87 noble gas analyses of CI and CM (Schultz and  
201 Franke, 2004). The H, C and N data are from 40 analyses compiled by Kerridge (1985). The

202 respective mean chondritic abundances of C, N, H<sub>2</sub>O and <sup>36</sup>Ar are, in mol/g: 2.3±1.2 x 10<sup>-3</sup>, 6.4±2.5 x  
203 10<sup>-5</sup>, 3.7±1.0 x 10<sup>-3</sup> and 3.1±1.6 x 10<sup>-11</sup>, respectively.

### 204 2.3 Earth

205 The inventory of volatile elements at the Earth's surface (the atmosphere, the oceans and the crust)  
206 is reasonably well known. The problem is to estimate the amount of volatiles in the mantle, since  
207 magmas tend to degas readily upon eruption, and the inferred source compositions are model-  
208 dependent. Recent estimates of the bulk Earth (mantle plus surface) volatile inventories have been  
209 given by Marty (2012), Halliday (2013) and Dauphas and Morbidelli (2014). We adopt here two  
210 limiting cases. The lower limit is based on the reconstruction of the initial volatile inventory of the  
211 mantle regions sampled by volcanism. The initial contents of water, C, N and noble gases in the  
212 mantle source of mid-ocean ridge basalts (MORB; volumetrically the main source of lavas at the  
213 Earth's surface) is derived from a combination of lava fluxes and calibration to relevant tracers like  
214 <sup>3</sup>He or refractory elements like Ce, Nb. Halliday (2013) considered also the source of Ocean Island  
215 basalts (another important source of volcanism thought to tap deep regions of the mantle), ("HA" in  
216 Figs. 3 and 4). Dauphas and Morbidelli (2014; "DM") obtained an inventory comparable to the one  
217 of Halliday (2013) from global calibration of volatiles to refractory (Ce, Nb) elements, and obtained  
218 a total bulk Earth water content of about 3 ocean masses ( $M_{\text{Ocean}}$  equivalent to 230 ppm H<sub>2</sub>O for bulk  
219 Earth). The isotopic compositions of helium, neon, argon and xenon suggest that deep mantle regions  
220 could be richer in volatiles than the convective mantle sampled by mid-ocean ridges. K-Ar  
221 systematics indicate that about half of radiogenic <sup>40</sup>Ar produced in Earth over 4.5 Ga is still trapped  
222 in the solid Earth, the rest having been degassed into the atmosphere (Allègre et al., 1996).  
223 Calibrating volatile elements to <sup>40</sup>Ar trapped in the mantle led Marty (2012) to propose a bulk mantle  
224 ("MA") higher than the above estimates, corresponding to 4-10 ocean masses. This approach does  
225 not rely on models of the structure and the composition of mantle domains. However, it assumes a  
226 chondritic composition for Terrestrial refractory elements. This is because the potassium content of

227 the Earth (Arevalo et al., 2009) is calibrated against refractory uranium as potassium is semi-volatile  
228 and its abundance cannot be retrieved from meteoritic analogs. A chondritic Earth composition for  
229 refractory elements has been recently questioned on the basis of sub-chondritic Terrestrial Nd  
230 isotope ratios, with the possibility that up to half of U, and therefore K, could have been stripped off  
231 by impacts on a differentiated Earth (e.g., Jellinek and Jackson, 2015; and refs. therein). This would  
232 reduce the  $^{40}\text{Ar}$  inventory and therefore allow much lower volatile contents. For this reason, we  
233 consider that the MA inventory of Table 4 gives an upper limit for the Terrestrial volatile budget.

### 234 **3. Discussion**

#### 235 *3.1. How representative are cometary data?*

236 We assume here that 67P data on one hand, and available cometary data on another hand, are  
237 representative of the composition of icy bodies that scattered in the inner solar system. This  
238 assumption is certainly fragile in the sense that key species measured in 67P coma are likely to vary  
239 from comet to comet. However, comets formed probably from comparable building material, water  
240 and other ice species making ~30-50 % of total mass. For most volatile species given in Tables 2 and  
241 3, measurements were done spectroscopically on several comets (Mumma and Charnley, 2011,  
242 Bockelée-Morvan, 2011, Le Roy et al., 2015) so the large range of observed values is considered to  
243 be representative of the natural variability.

244 For noble gases, the Ar measurement of Balsiger et al. (2015) is the only available set of data, but  
245 we propose below that the range of observed values is representative of the coma composition.  
246 Fractionation of a minor, low temperature species/element like argon relative to  $\text{H}_2\text{O}$  can range over  
247 1-2 order(s) of magnitude, depending on its sublimation temperature relative to that of  $\text{H}_2\text{O}$  ice.  
248 Marboeuf and Schmitt (2014) modeled fractional degassing of cometary volatiles as a function of the  
249 distance to the perihelion, under a range of different assumptions concerning the thermal inertia of a  
250 comet, the nature of ice, and the abundance and distribution of the different volatile species. Argon

251 was not considered in their study, so we take as a proxy CO which has a comparable  
252 condensation/sublimation temperature. Results of their modeling indicate that, at a distance between  
253 3 and 4 AU from the perihelion, the CO/H<sub>2</sub>O ratio of the coma is comparable to that of the bulk  
254 comet. Argon measurements by the ROSINA mass spectrometer were done on October 19, 20, 22,  
255 and 23, 2014 when Comet 67P was at ~3.1 AU from the Sun, thus possibly minimizing fractionation  
256 of minor species like Ar relative to H<sub>2</sub>O. The 67P <sup>36</sup>Ar/H<sub>2</sub>O ratio of 0.1-2.3 x 10<sup>-5</sup> is also comparable  
257 to, although lower than, ratios predicted from modeling of ice trapping experiment data (2-40 x 10<sup>-5</sup>  
258 in the 30-45 K range according to Dauphas, 2003; 8-75 x 10<sup>-5</sup> according to Marty and Meibom, 2007,  
259 based on experimental data from Notesco and Bar-Nun, 2005). Models and experiments of noble gas  
260 trapping into cometary ice indicate that the main controlling factors on the abundance of trapped  
261 noble gases are the temperature and the partial pressures of gases (Bar-Nun et al., 1985; Yokochi et  
262 al., 2012), so that other parameters of comet formation being equal, we assume that the Ar content of  
263 cometary matter is represented by 67P data. Although the above assumptions may constitute the  
264 main weak point of the present approach, we note that uncertainty range covers one order of  
265 magnitude of the stated values (the <sup>36</sup>Ar/H<sub>2</sub>O ratio) whereas the present conclusions here are based on  
266 variations of key parameters over several orders of magnitude.

### 267 3.2. *Impact driven atmospheric loss*

268 The present approach assumes that impacts are conservative, that is, contributed volatiles and  
269 target volatiles are not lost into space. This was likely not the case since giant impacts probably led  
270 to significant atmospheric loss (e.g., Genda and Abe, 2005). Recent models argue for a steady state  
271 regime between replenishment and atmospheric escape, depending on velocities, atmospheric entry  
272 angles, and sizes of impacting bodies (De Niem et al., 2012; Schlichting et al., 2014), but modeling  
273 the overall budget of volatile loss/gain is presently out of reach. Instead, we turn to a mass balance  
274 approach involving radiogenic <sup>129</sup>Xe, produced from the extinct radioactivity of iodine-129 (T<sub>1/2</sub> = 16  
275 Ma). Iodine was present when the Earth formed, as shown by the occurrence on Earth of the stable

276 isotope  $^{127}\text{I}$ . From meteoritic studies, it is possible to derive the solar system initial  $^{129}\text{I}/^{127}\text{I}$  ( $1.0 \times 10^{-4}$ ).  
277  $^{129}\text{I}$  was still alive, then terrestrial reservoirs should present excesses of  
278  $^{129}\text{Xe}$  produced by the decay of  $^{129}\text{I}$ . This is the case as an excess of 7%  $^{129}\text{Xe}$  (the main reservoir of  
279 terrestrial xenon) is present in air. This excess corresponds to about 1-2 % of  $^{129}\text{Xe}$  that could have  
280 been present if the Earth formed at the start of solar system formation. Assuming that produced  $^{129}\text{Xe}$   
281 was lost before the atmosphere became closed for volatile escape, one obtains a I-Xe closure age of  
282  $\sim 100$  Ma after start of Solar System formation for the terrestrial system (Wetherill 1980).  
283 Atmospheric xenon including  $^{129}\text{Xe}$  might have been escaping from the terrestrial atmosphere for  
284 prolonged periods of time, possibly during about 2 Ga (Pujol et al., 2011), so that the  $^{129}\text{Xe}$  excess  
285 has to be corrected for subsequent loss of atmospheric Xe. After correction, the closure age of the  
286 atmosphere becomes 30-60 Ma (Avice and Marty, 2014). A comparable budget arises when  
287 combining extinct radioactivities of  $^{129}\text{I}$  and  $^{244}\text{Pu}$  ( $T_{1/2} = 82$  Ma), implying that Xe loss was early,  
288 within a few tens of Ma after start of Solar System formation. Thus, according to I-Pu-Xe mass  
289 balance, early atmospheric loss, presumably during the proto-Earth building epoch, might not have  
290 exceeded 60-80 % of atmospheric Xe, and probably less after the Moon-forming impact which  
291 occurred within 40-90 Ma after start of Solar System formation. We tentatively conclude that the  
292 atmosphere was grossly conservative, within a factor of two, after the Moon-forming impact (the  
293 period of time relevant to cometary contributions, see next sub-sections).

### 294 *3.3. Origin of major volatile species on Earth*

295 The Ar content of cometary material inferred from the analysis of argon in 67P coma is 3-4 orders  
296 of magnitude higher than the one of chondritic material, which makes Ar, and by inference other  
297 heavy noble gases, a key tracer of cometary contribution to Earth. Together with the D/H ratio, the  
298 ratio between argon and  $\text{H}_2\text{O}$ , C and N permits to establish firm constraints on the contribution of  
299 67P-like material to Terrestrial volatiles. Swindle and Kring (2001) considered the ratio between  $^{36}\text{Ar}$   
300 and  $\text{H}_2\text{O}$  in comets (they took the Hale Bopp's  $^{36}\text{Ar}/\text{O}$  ratio from Stern et al., 2000, which has been

301 questioned since then) to infer an extremely low contribution of cometary material to the surfaces of  
302 Earth and Mars. Dauphas (2003) noted that the low Xe/H<sub>2</sub>O ratio of the Earth compared to other  
303 cosmochemical end-members could set stringent constraints on the maximum amount of cometary  
304 water on Earth. Since then, it has been proposed that the low terrestrial Xe/H<sub>2</sub>O ratio could be  
305 secondary (Pujol et al., 2011), making the argument less constraining. Figs. 3 and 4 represent mixing  
306 curves between chondritic and cometary end-members using the <sup>36</sup>Ar/X (where X represents water,  
307 nitrogen or carbon) ratio versus the D/H ratio. In fact the <sup>36</sup>Ar concentration is more sensitive than  
308 the D/H ratio alone, because contribution of 67P-like material can strongly impact the atmospheric  
309 inventory of argon. For water, a cometary contribution of the order of 1% or less is allowed  
310 depending on the bulk silicate Earth + surface composition (Fig. 3a), confirming that Terrestrial  
311 water is mostly non-cometary. A comparable conclusion arises for nitrogen (Fig. 3b), although a  
312 larger cometary contribution up to a few percent is allowed, due to the depletion of N in Earth  
313 (Marty, 2012). Nitrogen isotopes may permit to get independent constraints because spectroscopic  
314 measurements on comets indicate that the measured N-bearing species, CN, HCN and NH<sub>2</sub> (the latter  
315 presumably from NH<sub>3</sub>) are all enriched by a factor of 2 in <sup>15</sup>N relative to <sup>14</sup>N (e.g., Füri and Marty,  
316 2015, for a review). However, other N species like N<sub>2</sub> (Rubin et al., 2015) and refractory organics are  
317 present in comets with unknown N isotope composition, preventing to establish an isotope budget for  
318 the cometary reservoir.

319 Based on the same approach, Terrestrial carbon appears to originate from chondrite-like material  
320 (Fig. 4a), with a possible cometary contribution being lower than ~1 %. This conclusion stands even  
321 when considering that cometary carbon may be hosted not only in ice but also in refractory organics  
322 from the nucleus.

### 323 *3.4. Possible cometary origin for atmospheric noble gases*

324 Contrary to major volatiles, the mixing diagram of Fig. 4b suggests that atmospheric argon, and  
325 by extension other heavy noble gases, could originate from a cometary reservoir, a possibility

326 already proposed by Anders and Owen (1977) and Owen and Bar-Nun (1995) based on the noble gas  
327 abundance pattern of the atmosphere, and by Marty and Meibom (2007) from mass balance  
328 considerations. For the bulk silicate Earth inventory, the conclusion depends on the adopted  
329 composition. For the HA and DM inventories, a major cometary origin for argon is clearly possible  
330 (Fig. 4b). The MA inventory does not require contribution of cometary noble gases to the bulk Earth  
331 (Fig. 4b). In this model, noble gases are mostly in the atmosphere, and major volatiles (H<sub>2</sub>O, C) are  
332 in the mantle, the sum of which being consistent with the addition of ~ 2 wt. % of carbonaceous  
333 chondrite type material.

### 334 *3.5. Potential cometary contribution during the major bombardment periods*

335 Here we examine possibilities of a cometary contribution from the dynamical point of view. From  
336 solar system dynamics and isotope cosmochemistry, the major events that contributed potentially wet  
337 material to the building of Earth are:

338 1- Contribution of wet bodies to the growing proto-Earth (Morbidelli et al., 2000; Raymond et al.,  
339 2004; O'Brien et al., 2006, 2014). Dry material in the Terrestrial region became scarce as a result of  
340 accretion to larger bodies, leaving space to wet contributions from larger heliocentric distances.  
341 These late contributions should have consisted of volatile-rich asteroids, rather than comets. In line  
342 with this, krypton (Holland et al., 2009), hydrogen and nitrogen isotopes (Alexander et al., 2012;  
343 Marty, 2012) point to a chondritic, rather than cometary, source for contributed volatiles that are now  
344 stored in the Terrestrial mantle (Fig. 2).

345 2- The giant impact that led to the Moon formation. It is not clear if this event resulted or not in a  
346 major loss of volatile elements the proto-Earth. Already existing atmosphere and oceans could have  
347 survived the event (Genda and Abe, 2005), and/or the impactor could have contributed volatiles to  
348 the Earth-Moon system. From key isotope signatures (e.g., oxygen), the impactor was likely to  
349 originate from the inner solar system, and a cometary contribution is not considered further.

350 3- A late veneer (LV) might have supplied chondritic material after the last equilibration of  
351 mantle material with the core, presumably after the Moon forming impact (Kimura et al., 1974). Its  
352 contribution is estimated to be 0.3 wt. % (range 0.1-0.8 %) of the Terrestrial mass (Righter, 2003),  
353 that is,  $\sim 2 \times 10^{25}$  g. According to dynamical models, the LV was made of planetesimal leftover from  
354 the Terrestrial planet formation, without contribution of comets (Bottke et al., 2010; Raymond et al.  
355 2013; Morbidelli et al., 2012; Jacobson et al., 2014). In line with this view, a 100% cometary LV  
356 (Fig. 5a) contributing 0.3 % of the Terrestrial mass would supply too much atmospheric  $^{36}\text{Ar}$  by 2-3  
357 orders of magnitude, and would have dominated the H, C and N inventory, which is unlikely. A  
358 cometary contribution of 1 % or less could account for atmospheric Ar without impacting the stable  
359 isotope signatures (Fig 5b).

360 4- The Terrestrial late heavy bombardment (TLHB) is an extrapolation of the late heavy  
361 bombardment thought to have occurred on the Moon from the size-age distribution of lunar craters  
362 (Tera et al., 1974). Estimates of the mass contribution to Earth during the TLHB, based on the Lunar  
363 cratering record, range from  $2.2 \times 10^{23}$  g (Hartmann et al., 2002) down to  $4 \times 10^{22}$  g (assuming that  
364 the TLHB started at the time of formation of Nectaris basin; Morbidelli et al., 2012). From a  
365 modeling approach, Levison et al. (2001) proposed a mass contribution of  $8 \times 10^{22}$  g. Gomes et al.  
366 (2005) estimated a TLHB of  $4 \times 10^{23}$  g, about half of which being cometary. The newest version of  
367 the Nice model, however, reduces the mass flux to the Earth to about  $4 \times 10^{22}$  g of asteroidal material  
368 (Bottke et al., 2012) and  $2\text{-}4 \times 10^{22}$  g of cometary material (depending on the dynamical state of the  
369 trans-Neptunian disk before the dynamical instability). For the calculations presented here, a  
370 conservative value of  $2.0 \times 10^{23}$  g is adopted. Marty and Meibom (2007) concluded that less than 1 %  
371 comets were present in the TLHB, the rest being asteroidal material, and proposed that atmospheric  
372 noble gases could constitute the only remaining evidence for the TLHB. Their mass balance was  
373 based on noble gas cometary concentration from ice trapping experiments, which are higher than the  
374 one constrained by Ar in 67P. With the ROSINA  $^{36}\text{Ar}$  measurement, a 100% cometary TLHB would  
375 supply too much  $^{36}\text{Ar}$  to the atmosphere (Fig. 5c). It would also supply most major volatiles at the



376 Earth's surface, which is not allowed by the D/H and  $^{15}\text{N}/^{14}\text{N}$  ratios of the atmosphere and oceans. A  
377 cometary fraction of  $\sim 10\%$  in the TLHB accounts reasonably well for atmospheric  $^{36}\text{Ar}$  without  
378 impacting the stable isotope budget (Fig. 5d). Thus a cometary contribution of  $\sim 2.0 \times 10^{22}$  g respects  
379 our mass balance and is in excellent agreement with the latest model results.

380 5- The post TLHB continuous flux of interplanetary dust particles (IDPs), and micrometeorites is  
381 estimated at  $\sim 2 \times 10^{20}$  g, assuming a constant flux comparable to modern one (about 30,000 tons/yr,  
382 Love and Brownlee, 1993). A near-constant flux (with a possible factor of 5 increase in the last 0.5  
383 Ga) is consistent with the lunar soil record of extraterrestrial material (Culler et al., 2000; Hashizume  
384 et al., 2002). From the analysis of IDPs, this flux consists of both cometary and asteroidal materials.  
385 A 100% continuous IDP flux would not impact the volatile inventory of the Earth's surface including  
386 noble gases, even when this flux is increased by a factor of 5 (Fig. 5e).

### 387 *3.6. Further evidence for heterogeneous sources of noble gases on Earth*

388 From isotope geochemistry considerations, several distinct cosmochemical sources contributed  
389 noble gases to the growing Earth.

390 (i) Solar neon has been identified in the mantle (Honda et al., 1991). It does not necessarily imply a  
391 solar origin for heavier noble gases because the solar component is rich in light noble gases  
392 compared to Chondritic, so that mixing between Solar and Chondritic may impact light noble  
393 gases only. Neon is unlikely to have been trapped in cometary ice given its elevated condensation  
394 temperature.

395 (ii) The isotopic compositions of H, N and mantle Kr isotopes are consistent with a chondritic  
396 source.

397 (iii) Atmospheric xenon is unique in the solar system and cannot be derived directly from Solar or  
398 Chondritic. The light Xe isotopes are isotopically fractionated (depleted) by 3-4 %/amu relative to

399 cosmochemical Xe (either Solar or Chondritic). However this mass fractionation may be  
400 secondary and may not be a source signature (Pujol et al., 2011; Avive and Marty, 2014). Even  
401 when corrected for mass-dependent fractionation, the atmospheric Xe isotope composition cannot  
402 be derived from either Solar or Chondritic, because it is depleted in the heavy isotopes  $^{134}\text{Xe}$  and  
403  $^{136}\text{Xe}$  relative to the latter. Secondary (nuclear) processes such as fission of heavy radionuclides  
404 can only enrich, and not deplete, these isotopes. This observation led Takaoka (1972) and Pepin  
405 (1991) to postulate the existence of a distinct primordial Xe having sourced the Terrestrial  
406 atmosphere (the Xe-U component of Pepin, 1991). This mass-independent isotope fractionation of  
407 Xe isotopes might have resulted from an unknown nuclear effect, or from a different mix of  
408 nucleosynthetic components that were not fully homogenized during solar system formation.

409 Given the possible cometary origin of atmospheric noble gases, we speculate that this exotic Xe  
410 component could have been carried out from the outer solar system to its inner region by icy bodies.  
411 The dichotomy between mantle chondritic Xe and surface Xe would then be a record of Terrestrial  
412 growth, with the Proto-Earth being built from chondritic-like material, and its surface having been  
413 subsequently contributed by cometary bodies. In order to supply all atmospheric  $^{36}\text{Ar}$  ( $5.55 \times 10^{15}$   
414 moles, Ozima and Podosek, 2002), a cometary contribution between  $3 \times 10^{21}$  and  $6.5 \times 10^{23}$  g would  
415 have been necessary (computed with a  $^{36}\text{Ar}$  cometary concentration of  $2.1 \pm 1.9 \times 10^{-7}$  mol/g, and a  
416 cometary density of 0.5 from the 67P measurements). This is in great agreement with the most recent  
417 estimates of the cometary flux to the Earth during the TLHB. Thus, there is no “missing comet  
418 bombardment” unlike the earlier conclusions of Marty and Meibom (2007) based on an higher  $^{36}\text{Ar}$   
419 content of comets. The impact of a single cometary body with a radius of 100-300 km, or of a limited  
420 number of smaller bodies, could have sufficient to supply all atmospheric argon. Therefore, it may be  
421 possible that the supply of atmospheric volatiles to the Terrestrial planets was a stochastic process  
422 involving a small population of objects, which might have resulted in an heterogeneous distribution  
423 of outer solar system isotopic signatures. In this respect, the high abundance of  $^{36}\text{Ar}$  in the

424 atmosphere of Venus could effectively be the result of random contribution of cometary material to  
425 inner planets.

### 426 *3.7. Origin of prebiotic material on Earth constrained from atmospheric argon*

427 Peptide synthesis from amino-acids appears a necessary step for the development of prebiotic  
428 material on Earth. Although a number of possible scenarios invoking catalytic reactions in specific  
429 Terrestrial environments have been advanced, it has also been proposed that impacts could have  
430 favored peptide synthesis from ET amino-acids (Blank et al., 2001). Sugahara and Mimura (2014)  
431 simulated comet impacts by shock experiments at low temperature in the range 5-26 GPa and found  
432 that linear peptide synthesis up to tripeptide forms could be achieved only with initially low  
433 temperature. As formation of linear peptide appears a key process for further elongation of peptide  
434 chains, these authors argued that comet impacts might have played a key role in the formation of  
435 prebiotic material on Earth. An upper limit for the total delivery of potential prebiotic material to  
436 Earth by comets can be set by considering that all atmospheric  $^{36}\text{Ar}$  was delivered by icy bodies to  
437 the Earth's surface. Carbonaceous chondrites contain about 80 different amino-acids (Ehrenfreund  
438 and Charnley, 2000), with their total concentration amounting for 250 ppm (e.g., Martins et al.,  
439 2007). Their concentration in cometary matter is unknown. Studies of Stardust cometary grains  
440 suggest similarities with stratospheric IDPs and carbonaceous chondrites (Brownlee et al., 2006).  
441 Thus, for the purpose of illustration, we consider that the carbonaceous chondrite concentration is  
442 representative of cometary matter. The mass of cometary material having the  $^{36}\text{Ar}$  content of 67P  
443 ( $2.1 \pm 1.9 \times 10^{-7}$  mol/g) that would have delivered atmospheric  $^{36}\text{Ar}$  ( $5.55 \times 10^{15}$  moles) is  $0.2\text{-}5 \times 10^{22}$   
444 g, leading to the delivery of  $0.6\text{-}13 \times 10^{18}$  g of amino acid-rich material. This amount is comparable  
445 to the present-day mass of the biosphere ( $\sim 2 \times 10^{18}$  g). With the present-day mass of the oceans,  
446 comets could have delivered up to 10-40 ppm prebiotic material to seawater. Thus depending on the  
447 efficiency of survival and of peptide synthesis upon impact, comets might have contributed non-  
448 negligible prebiotic material during the TLHB.

449 3.8. *The case of the Martian atmosphere*

450 The composition of the atmosphere of Mars (Table 4) is reasonably known from the in-situ  
451 analyses by the Viking and the Mars Science Laboratory (MSL) landers, and from the analysis of  
452 some of the Martian meteorites which contain atmospheric volatiles trapped in impact glasses (see  
453 Bogard et al., 2001, for a comprehensive review, and Wong et al., 2013, and refs. therein, for recent  
454 Curiosity MSL data). Compared to Earth and bulk meteorites, the Martian atmosphere is rich in  $^{15}\text{N}$   
455 ( $\delta^{15}\text{N} = 572 \pm 82 \text{‰}$  relative to the Terrestrial atmosphere, Wong et al., 2013) and in deuterium ( $\delta\text{D} =$   
456  $5,500 \text{‰}$  relative to the oceans; Bogard et al., 2001; Montmessin et al., 2005, and refs therein; Fig.  
457 2). Likewise, neon, argon ( $^{36}\text{Ar}$ ,  $^{38}\text{Ar}$ ) and xenon isotopic signatures are enriched in their heavy  
458 isotopes by 246, 151, and 33 ‰, respectively, relative to the solar compositions (Table 4). In  
459 contrast, volatiles in the Mars interior, also analyzed in Martian meteorites, have isotopic ratios  
460 comparable to inner solar system signatures (Fig. 2).

461 The atmospheric signatures have been interpreted as resulting from isotope fractionation during  
462 atmospheric escape processes. Possibilities include solar wind-induced photochemical reactions  
463 producing electrons able to dissociate  $\text{N}_2$  for nitrogen (Mc Elroy et al., 1976), and sputtering for the  
464 noble gases (Jakosky et al., 1994). Chassefière and Leblanc (2004) reviewed potential escape  
465 mechanisms that might have affected the atmosphere of Mars and concluded that (i) not a single  
466 process can account for the observations; and (ii) non-thermal processes are required and therefore  
467 might have affected different atoms/species at variable levels independently of their masses.  
468 Atmospheric loss is attested by morphological evidence on Mars indicating past water flows (Carr  
469 and Head, 2003), and major escape processes might have taken towards the end of the Noachian  
470 period 4.0-3.7 Ga ago. Thus escape-related fractionation of Martian volatiles is likely to have played  
471 a key role in fractionating elemental abundances and isotopic compositions. Nevertheless, we  
472 suggest here that possible source effects, namely cometary contributions, should be also considered,  
473 especially after the major escape events that resulted in a tenuous atmosphere on Mars.

474 Several key observations are not entirely consistent with atmospheric escape as a cause of isotopic  
475 enrichments. (i) The noble gas elemental abundance of the Martian atmosphere and the C/N ratio  
476 (Pepin, 1991) are comparable to those of Venus and Earth (for which similar escape fractionations  
477 are unlikely). (ii) The krypton isotopic composition of the Martian atmosphere is close to the solar  
478 composition (Bogard et al., 2001, and refs. therein), contrary to those of Ne, Ar and Xe (Table 4).  
479 Because the mass of Kr is intermediate between those of Ne, Ar and Xe, this difference points to other  
480 processes than escape-related fractionation. We note that the Martian Ne isotopic composition is  
481 within the range of chondritic values, e.g., the so-called Ne-A (planetary) component of  
482 carbonaceous chondrites. Neon is not expected to be trapped in comets, so that Martian atmospheric  
483 Ne could have been sourced by an another cosmochemical reservoir. The high  $^{38}\text{Ar}/^{36}\text{Ar}$  ratio ( $0.238$   
484  $\pm 0.005$ ; Atreya et al., 2013) is indeed a good diagnostic of escape-related fractionation, but cosmic-  
485 ray production of noble gas isotopes (which also increases this ratio) could have been significant for  
486 the tenuous Martian atmosphere. Such effects need to be assessed. The Xe isotope fractionation  
487 could have arisen from a Xe-specific non-thermal escape process, like the one proposed for  
488 Terrestrial atmospheric Xe (Pujol et al., 2011). (iv) The isotopes of C, O, S in the Martian surface  
489 and crust are little fractionated.  $\text{CO}_2$  is enriched in  $^{13}\text{C}$  relative to Terrestrial ( $\delta^{13}\text{C} = 46 \pm 4 \text{‰}$ ;  
490 Mahaffy et al., 2013) but to a much lesser extent than  $^{15}\text{N}$  in nitrogen ( $\delta^{15}\text{N} = 572 \pm 82 \text{‰}$ , Wong et al.,  
491 2013). However this argument is not carved in stone since C, O, S isotope compositions might have  
492 been buffered by crustal reservoirs.

493 We suggest that some of the Martian atmospheric characteristics are consistent with a cometary  
494 origin. This possibility was proposed by Owen and Bar-Nun (1995) who noted  $^{36}\text{Ar}/^{84}\text{Kr}/^{132}\text{Xe}$   
495 similarities between the Earth and Mars despite large differences in atmospheric pressures,  
496 suggesting that a non-fractionating process supplied atmospheric noble gases to both planets. They  
497 argued that the Martian  $^{36}\text{Ar}/^{84}\text{Kr}/^{132}\text{Xe}$  ratios resemble to those obtained in experimentally grown  
498 ice, and proposed impacts of icy planetesimals as the source of Martian surface volatiles. Although  
499 we do not think that the Xe abundance pattern and its isotopic composition are cometary (the Martian

500 Xe fractionation could result from Xe-specific non-thermal processing like on Earth, Pujol et al.,  
501 2011), we test below a possible cometary contribution by using other volatile element signatures.

502 First, in a N vs. H isotope diagram, the atmosphere of Mars plots close to the field of comets (Fig.  
503 2). Second, the Martian C/N, C/<sup>36</sup>Ar and N/<sup>36</sup>Ar ratios are all close within a factor of 2 to our estimate  
504 for cometary composition (and to Earth's surface inventory, Table 4, Fig. 6), whereas the C/<sup>36</sup>Ar and  
505 N/<sup>36</sup>Ar ratios are markedly different from the chondritic values (Table 4). The δ<sup>15</sup>N vs. <sup>36</sup>Ar/N<sub>2</sub>  
506 isotope variations are consistent with a two-component mixing (Fig. 7). In this format, mixings  
507 define straight lines (curves in the semi-log diagram of Fig. 7). Both the Martian atmosphere's δ<sup>15</sup>N  
508 and <sup>36</sup>Ar/N<sub>2</sub> values are within the estimated range of cometary ratios, and variations observed in  
509 Martian meteorites define another end-member having lower δ<sup>15</sup>N and higher <sup>36</sup>Ar/N<sub>2</sub> ratios, that  
510 could be chondritic and/or terrestrial contamination (preferential adsorption of nitrogen relative to  
511 argon). The Kr isotope composition is solar-like, as expected for a cometary origin. After correction  
512 for mass-dependent fractionation, Xe is also isotopically solar (Pepin, 1991).

513 We then explore the possibility of a cometary contribution by scaling potential cometary fluxes on  
514 Earth to the dimensions of Mars. In Fig. 6, the impacting fluxes on Earth have been adapted to the  
515 Martian dimensions by dividing them by a factor of ~5. This factor is obtained from the ratio of  
516 planetary surfaces (3.5 for Earth/Mars) plus a gravitational focusing effect of ~1.5. It comes out that  
517 a Martian late veneer would supply far too much cometary volatiles to Mars (Fig. 6). For a TLHB  
518 total (asteroidal+ cometary) flux of ~2 x 10<sup>23</sup> g, the total Martian LHB (M-LHB) flux would be ~5 x  
519 10<sup>22</sup> g. Ten % comet in the M-LHB as on Earth gives a cometary flux on Mars of ~5 x 10<sup>21</sup> g, which  
520 is remarkably comparable to the range of 7-14 x 10<sup>21</sup> g obtained from recent simulations. However, a  
521 10% cometary M-LHB would add too much volatiles to Mars by ~1 order of magnitude (Fig. 6).  
522 Thus either the LHB flux was heterogeneous between Earth and Mars, or part of the Martian  
523 atmosphere was subsequently lost after M-LHB by atmospheric escape processes. In line with the  
524 second possibility, the D/H values of the Martian interior and Martian atmosphere are shifted

525 towards D-enrichments (right-hand side in Fig. 2) relative to inner solar system values defined by  
526 Earth and chondrites on one hand, and by comets on another hand. Thus the Martian D/H value is too  
527 high to be solely cometary, and it is likely that atmospheric escape processes played a role in  
528 fractionating hydrogen isotopes, and, possibly, other light species (neon ?). Finally, the continuous  
529 flux of IPDs on Mars could constitute a non-negligible source of cometary volatiles (Fig. 6), if made  
530 predominantly of cometary material. In line with this possibility, Fries et al (2016) proposed  
531 recently that "meteor showers" made of cometary debris could account for the presence of methane  
532 in the Martian atmosphere.

#### 533 **4. Conclusions and outlook**

534 The in-situ analysis of coma from comet 67P together with remote sensing data from other comets  
535 gives semi-quantitative constraints on the origin of volatile elements in Terrestrial planets.  
536 Particularly important is the discovery of significant amounts of primordial argon in the coma of  
537 67P, well above the level observed in primitive meteorites.

538 For Earth, the major volatiles documented here - H<sub>2</sub>O, C, N - were sourced mostly by material  
539 akin of wet asteroids. Only a few percents at most of water, carbon and nitrogen could have  
540 originated from comet-like bodies. However the terrestrial atmosphere could contain a significant,  
541 possibly dominant, fraction of cometary noble gases, which might have been delivered during the  
542 Terrestrial Late Heavy Bombardment around 4 Ga ago. This possibility is in line with dynamical  
543 models of solar system evolution, which predict a significant fraction of icy bodies in the TLHB.  
544 Resolving this question will require a better estimate of the volatile element inventory of the Earth.  
545 Models that ascribe a "low" volatile content of our planet (Halliday, 2013; Dauphas and Morbidelli,  
546 2014) imply that atmospheric noble gases are cometary, whereas the "high" volatile content model  
547 (Marty, 2012) does not require comets and is consistent with a predominantly asteroidal (chondritic)  
548 source (see Fig. 4b). A chondritic, rather than cometary, origin for atmospheric noble gases is  
549 independently consistent with Ne-Ar isotope variations among the major terrestrial reservoirs

550 including the atmosphere (Marty, 2012). This problem may appear too specialized for a non-  
551 specialist audience, but there are outstanding issues beyond it, such as the origin of prebiotic material  
552 on Earth (which could be traced with noble gases), the early processes of volatile delivery and  
553 escape, the timing of volatile delivery (which can be addressed with noble gas radiogenic isotopes),  
554 and the composition and mode of transfer of material from the outskirts of the Solar System. For  
555 example, the isotopic composition of atmospheric xenon cannot be simply related to either the solar  
556 nebula or asteroidal material. It requires a specific composition (U-Xe; Pepin, 1991) that could trace  
557 nucleosynthetic heterogeneities in outer solar system bodies. Resolving these important issues will  
558 require a better estimate of the volatile content of the mantle on the one hand, as well as precise  
559 cometary noble gas data including isotopes on the other hand.

560 A cometary contribution to Martian surface volatiles (nitrogen and noble gases) appears clearly  
561 possible, given our present state of knowledge, and is consistent with solar system dynamical  
562 models. However, the strong deuterium enrichment of the Martian surface can hardly be the result of  
563 a cometary contribution, and requires isotope fractionation during escape processes at least for these  
564 light species. Resolving source effects versus processing is a major challenge that will require, as for  
565 the Earth, a better knowledge of the Martian and cometary signatures for major and minor volatile  
566 species.

567 The volatile characteristics of the inner planets are consistent with trapping of protosolar nebula  
568 gas during early stages on accretion, and contributions from wet bodies from increasing heliocentric  
569 distance during the sequence of planetary building and late accretion. However no unified picture  
570 emerges for the origin(s) and processes of delivery of inner planets' atmospheric volatiles. What are  
571 now highly needed are measurements of the noble gas abundances in comets and the isotopic ratios  
572 of neon, krypton and most importantly xenon. Such measurements should be given a high priority in  
573 future cometary missions. The requested level of precision (better than percent for noble gas isotopic



574 ratios, and per mil for stable isotopes including the three isotopes of oxygen) will require a cometary  
575 sample return mission to permit laboratory analysis.

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591 **References**

- 592 A'Hearn, M., et al. 2011. EPOXI at Comet Hartley 2. *Science* 332, 1396–1400.
- 593 Albarède, F., et al., 2013. Asteroidal Impacts and the Origin of Terrestrial and Lunar Volatiles.  
594 *Icarus* 222, 44-52.
- 595 Aléon, J., 2010. Multiple Origins of Nitrogen Isotopic Anomalies in Meteorites and Comets.  
596 *Astrophys. J.* 722, 1342-1351.
- 597 Alexander, C.M.O'D., et al., 2012. The Provenances of Asteroids, and Their Contributions to the  
598 Volatile Inventories of the Terrestrial Planets. *Science* 337, 721–23.
- 599 Allègre, C. J., Hofmann, A.W., O'Nions, R.K., 1996. The Argon Constraints on Mantle Structure.  
600 *Geophys. Res. Lett.* 23, 3555–57.
- 601 Altwegg, K., et al., 2015. 67P/Churyumov-Gerasimenko, a Jupiter Family Comet with a High D/H  
602 Ratio. *Science* 347, 1261952–1.
- 603 Anders, E., Owen, T., 1977. Mars and Earth Origin and Abundance of Volatiles. *Science* 198, 453–  
604 65.
- 605 Arevalo, R., McDonough, W., F., Luong, M., 2009. The K/U Ratio of the Silicate Earth: Insights into  
606 Mantle Composition, Structure and Thermal Evolution. *Earth Planet. Sci. Lett.* 278, 361–369.
- 607 Atreya, S., et al., 2013. Primordial Argon Isotope Fractionation in the Atmosphere of Mars Measured  
608 by the SAM Instrument on *Curiosity* and Implications for Atmospheric Loss. *Geophys. Res.*  
609 *Lett.* 40, 5605-5609.

610

- 611 Avice, G., Marty, B., 2014. The Iodine-Plutonium-Xenon Age of the Moon-Earth System Revisited.  
612 Phil. Trans. Ser. A, 372, 20130260.
- 613 Balsiger, H., et al., 2015. Detection of Argon in the Coma of Comet 67P/Churyumov-Gerasimenko.  
614 Science Adv. 10.1126/sciadv.1500377.
- 615 Bar-Nun, A., Herman, G., Laufer, D., Rappaport, M.L., 1985. Trapping and Release of Gases by  
616 Water Ice and Implications for Icy Bodies. *Icarus* 63, 317–332.
- 617 Blank, J.G., Miller, G.H., Ahrens, M.J., Winans, R.E., 2001. Experimental Shock Chemistry of  
618 Aqueous Amino Acid Solutions and the Cometary Delivery of Prebiotic Compounds. *Origins*  
619 *Life Evol. Biosph.* 31, 15–51.
- 620 Bockelée-Morvan, D., 2011. An Overview of Comet Composition. *Proceed. Intern. Astron. Union* 7,  
621 261–274.
- 622 Bogard, D.D., Clayton, R.N., Marti, K., Owen, T., Turner, T., 2001. Martian Volatiles: Isotopic  
623 Composition, Origin and Evolution. *Space Sci. Rev.* 96, 425-458.
- 624 Bottke, W.F., Walker, R.J., Day, J.M.D., Nesvorny, D., Elkins-Tanton, L., 2010. Stochastic Late  
625 Accretion to Earth, the Moon, and Mars. *Science* 330, 1527.
- 626 Bottke, W.F., et al., 2012. An Archaean Heavy Bombardment from a Destabilized Extension of the  
627 Asteroid Belt. *Nature* 485, 78–81.
- 628 Brownlee, D.L., et al., 2006. Comet 81P/Wild 2 under a Microscope. *Science* 314, 1711–1716.
- 629 Carr, M.H., Head, J.W., 2003. Oceans on Mars: An Assessment of the Observational Evidence and  
630 Possible Fate. *J. Geophys. Res.* 108, DOI: 10.1029/2002JE001963.
- 631 Chassefière, E., Leblanc, F., 2004. Mars Atmospheric Escape and Evolution: Interaction with the  
632 Solar Wind. *Planet. Space Sci.* 52, 1039-1058.

- 633 Chennaoui Aoudjehane, H., et al., 2012. Tissint Martian Meteorite: A Fresh Look at the Interior,  
634 Surface, and Atmosphere of Mars. *Science* 738, 785-788.
- 635 Chyba, C.F., 1990. Impact Delivery and Erosion of Planetary Oceans in the Inner Solar System.  
636 *Nature* 343, 129–133.
- 637 Culler, T.S., Becker, T.A., Muller, R.A., Renne, P.R., 2000. Lunar Impact History from Ar-40/Ar-39  
638 Dating of Glass Spherules. *Science* 287, 1785–188.
- 639 Dauphas, N., 2003. The Dual Origin of the Terrestrial Atmosphere. *Icarus* 165, 326–339.
- 640 Dauphas, N. and Morbidelli, A., 2014. Geochemical and Planetary Dynamical Views on the Origin  
641 of Earth' Atmosphere and Oceans. *Treatise Geochem.* 2nd Ed., 6, 1-35.
- 642 De Niem, D., Kührt, E., Morbidelli, A., Mutschmann, U., 2012. Atmospheric Erosion and  
643 Replenishment Induced by Impacts upon the Earth and Mars during a Heavy Bombardment.  
644 *Icarus* 221, 495–507.
- 645 Duprat, J., et al., 2010. Extreme Deuterium Excesses in Ultracarbonaceous Micrometeorites from  
646 Central Antractic Snow. *Science* 328, 742–745.
- 647 Ehrenfreund, P., Charnley, S.B., 2000. Organic Molecules in the Interstellar Medium, Comets, and  
648 Meteorites: A Voyage from Dark Clouds to the Early Earth. *Ann. Rev. Astron. Astrophys.* 38,  
649 427–483.
- 650 Fries, M., et al., (2016). A cometary origin for Martian Atmospheric Methane. *Geochem. Perspect.*  
651 *Lett.* 2, 10-23.
- 652 Füri, E., Marty, B., 2015. Nitrogen Isotope Variations in the Solar System. *Nature Geosci.* 8, 515–  
653 522.

- 654 Genda, H., Abe, Y., 2005. Enhanced Atmospheric Loss on Protoplanets at the Giant Impact Phase in  
655 the Presence of Oceans. *Nature* 433, 842–844.
- 656 Gomes, R., Levison, H.F., Tsiganis, K., Morbidelli, A., 2005. Origin of the Cataclysmic Late Heavy  
657 Bombardment Period of the Terrestrial Planets. *Nature* 435, 466–469.
- 658 Greenberg, J.M., 1998. Making a Comet Nucleus. *Astron. Astrophys.* 330, 375–380.
- 659 Halliday, A.N., 2013. The Origins of Volatiles in the Terrestrial Planets. *Geochim. Cosmochim. Acta*  
660 105, 146–171.
- 661 Hartmann, W.K., Ryder, G., Dones, L., Grinspoon, D., 2002. The Time-Dependent Intense  
662 Bombardment of the Primordial Earth/Moon System, in: *Origin of the Earth and Moon*, edited  
663 by: Canup, R. M. and Righter, K., Univ. Arizona Press, 493–451, 2002.
- 664 Hartogh, P., et al., 2011. Ocean-like Water in the Jupiter-Family Comet 103P/Hartley 2. *Nature* 478,  
665 218–220.
- 666 Hashizume, K., Marty, B., Wieler, R., 2002. Analyses of Nitrogen and Argon in Single Lunar  
667 Grains : Towards a Quantification of the Asteroidal Contribution to Planetary Surfaces. *Earth*  
668 *Planet. Sci. Lett.* 202, 201-216.
- 669 Hässig, M., et al., 2015. Time Variability and Heterogeneity in the Coma of 67P/Churyumov-  
670 Gerasimenko. *Science* 347, 6220, aaa0276–1-4.
- 671 Holland, G., Cassidy, M., Ballentine, C.J., 2009. Meteorite Kr in Earth’s Mantle Suggests a Late  
672 Accretionary Source for the Atmosphere. *Science* 326, 1522–1525.
- 673 Honda, M., McDougall, I.A., Patterson, D.B., , Doulgeris A., Clague, D.A., 1991. Possible Solar  
674 Noble-Gas Component in Hawaiian Basalts. *Nature* 349, 149–151.

675 Jacobson, S.A., Morbidelli, A., Raymond, S.N., O'Brien, D.P., Walsh, K.J., Rubie, D.C., 2014.  
676 Highly siderophile elements in Earth's mantle as a clock for the Moon-forming impact. *Nature*  
677 508, 84-87.

678 Jakosky, B.M., Pepin, R.O., Johnson R.E., Fox. J.L., 1994. Mars Atmospheric Loss and Isotopic  
679 Fractionation by Solar-wind-induced Sputtering and Photochemical Escape. *Icarus* 111, 271-  
680 281.

681 Jellinek, A.M., Jackson, M.G., 2015. Connections between the Bulk Composition, Geodynamics and  
682 Habitability of Earth. *Nature Geosci.* 8, 587–593.

683 Jessberger, E.K. , Cristoforidis E.A., Kissel, J., 1988. Aspects of the Major Elemental Composition  
684 of Halley's Dust. *Nature* 332, 691–695.

685 Kerridge, F., 1985. Carbon, Hydrogen and Nitrogen in Carbonaceous Chondrites: Abundances and  
686 Isotopic Compositions in Bulk Samples. *Geochim. Cosmochim. Acta* 49,1707–1714.

687 Kimura, K., Lewis, R.S., Anders, E., 1974. Distribution of Gold and Rhenium between Nickel-Iron  
688 and Silicate Melts - Implications for the Abundance of Siderophile Elements on Earth and  
689 Moon. *Geochim. Cosmochim. Acta* 38, 683–701.

690 Kissel J., Krueger, F.R., 1987. The Organic Component in Dust from Comet Halley as Measured by  
691 the PUMA Mass Spectrometer on Board Vega 1. *Nature* 326, 755–60.

692 Le Roy, L., et al., 2015. The volatile Inventory of Comet 67P/Churyumov-Gerasimenko from  
693 Rosetta/Rosina. *Astron. Astrophys.* Sept 9, 2015, DOI: 10.1051/0004-6361/201526450.

694 Levison, H.F., Dones, L., Chapman, C.R., Stern, A., 2001. Could the Lunar 'Late Heavy  
695 Bombardment' Have Been Triggered by the Formation of Uranus and Neptune? *Icarus* 151,  
696 286–306.

- 697 Love, S., Brownlee, D.E., 1993. A Direct Measurement of the Terrestrial Mass Accretion Rate of  
698 Cosmic Dust. *Science* 262, 550–553.
- 699 Mahaffy, P.R., et al., 2013. Abundance and Isotopic Composition of Gases in the Martian  
700 Atmosphere from the Curiosity Rover; *Science* 341, 263-266.
- 701 Marboeuf, U., Schmitt, B., 2014. How to Link the Relative Abundances of Gas Species in Coma of  
702 Comets to Their Initial Chemical Composition? *Icarus* 242, 225–248.
- 703 Marrocchi, Y., Marty, B., 2013. Experimental Determination of the Xenon Isotopic Fractionation  
704 During Adsorption. *Geophys. Res. Lett.* 40, 4165-4170.
- 705 Martins, Z., Botta, O., Ehrenfreund, P., 2007. Amino Acids in Antarctic CM1 Meteorites and Their  
706 Relationship to Other Carbonaceous Chondrites. *Meteorit. Planet. Sci.* 92, 81–92.
- 707 Marty, B., et al., 2008. Helium and Neon Abundances and Compositions in Cometary Matter.  
708 *Science* 319, 75–78.
- 709 Marty, B., 2012. The Origins and Concentrations of Water, Carbon, Nitrogen and Noble Gases on  
710 Earth. *Earth Planet. Sci. Lett.* 313-314, 56–66.
- 711 Marty, B., Meibom, A., 2007. Noble Gas Signature of the Late Heavy Bombardment in the Earth's  
712 Atmosphere. *eEarth* 2, 43–49.
- 713 Mc Elroy, M.B., Kong, T.Y., Yung, Y.L., 1977. Photochemistry and Evolution of Mars'  
714 Atmosphere: A Viking Perspective. *J. Geophys. Res.* 82, 4379-4388.
- 715 Montmessin, F., Fouchet, T., Forget, F., 2005. Modeling the annual cycle of HDO in the Martian  
716 atmosphere. *J. Geophys. Res.* 110: E03006.
- 717 Morbidelli, A., et al., 2000. Source Regions and Timescales for the Delivery of Water to the Earth.  
718 *Meteorit. Planet. Sci.* 35, 1309–1320.

719 Morbidelli, A., Marchi, S., Bottke, W.F., Kring, D.A., 2012. A sawtooth-like timeline for the first  
720 billion years of lunar bombardment. *Earth and Planetary Science Letters* 355, 144-151.

721 Mousis, O., et al., 2010. Impact Regimes and Post-formation Sequestration Processes: Implications  
722 for the Origin of Heavy Noble Gases in Terrestrial Planets. *Astrophys. J.* 714, 1418–1423.

723 Mumma, M.J., Charnley, S.B., 2011. The Chemical Composition of Comets - Emerging Taxonomies  
724 and Natal Heritage. *Ann. Rev. Astron. Astrophys.* 49, 471–524.

725 Notesco, G., Bar-Nun, A., 2005. A ~25 K Temperature Fo Formation for the Submicron Ice Grains  
726 Which Formed Comets. *Icarus* 175, 546–50.

727 O'Brien, D.P., Morbidelli, A., Levison, H.F. 2006. Terrestrial planet formation with strong  
728 dynamical friction. *Icarus* 184, 39-58.

729

730 O'Brien, D.P., Walsh, K.J., Morbidelli, A., Raymond, S.N., Mandell, A.M., 2014. Water delivery and  
731 giant impacts in the "Grand Tack" scenario. *Icarus* 239, 74-84.

732 Oro, J., 1961. Comets and the Formation of Biochemical Compounds on the Primitive Earth. *Nature*  
733 190, 389–390.

734 Ott, U., 2014. Planetary and Pre-Solar Noble Gases in Meteorites. *Chem. Erde*, 74, 519-544.

735 Owen, T., Bar-Nun, A., 1995. Comets, Impacts and Atmospheres. *Icarus* 116, 215-226.

736 Ozima, M., Podosek, F.A., 2002. Noble Gas Geochemistry. Cambridge University Press, 286 pp.

737 Pepin, R O., 1991. On the Origin and Early Evolution of Terrestrial Planet Atmospheres and  
738 Meteoritic Volatiles. *Icarus* 92, 2–79.

739 Porcelli, D., Ballentine, C.J., 2002. Models for the Distribution of Terrestrial Noble Gases and  
740 Evolution of the Atmosphere. *Rev. Mineral. Geochem* 47, 411-480.



741 Pujol, M., Marty, B., Burgess, R., 2011. Chondritic-like Xenon Trapped in Archean Rocks: A  
742 Possible Signature of the Ancient Atmosphere. *Earth Planet. Sci. Lett.* 308, 298–306.

743 Raymond, S.N., Quinn, T., Lunine, J.I., 2004. Making other earths: dynamical simulations of  
744 Terrestrial planet formation and water delivery. *Icarus* 168, 1-17.

745

746 Raymond, S.N., Quinn, T., Lunine, J.I., 2007. High-Resolution Simulations of The Final Assembly  
747 of Earth-Like Planets. 2. Water Delivery And Planetary Habitability. *Astrobiol.* 7, 66-84.

748

749 Raymond, S.N., Schlichting, H.E., Hersant, F., Selsis, F., 2013. Dynamical and collisional  
750 constraints on a stochastic late veneer on the Terrestrial planets. *Icarus* 226, 671-681.

751 Righter, K., 2003. Metal-Silicate Partitioning of Siderophile Elements and Core formation in the  
752 Early Earth. *Ann. Rev. Earth Planet. Sci.* 31, 135–74.

753 Rubin, M., et al., 2015. Molecular Nitrogen in Comet 67P/Churyumov-Gerasimenko Indicates a Low  
754 Formation Temperature. *Science* 348, 232-235. 1–4.

755 Safronov, V.S., 1972. The Motion, Evolution and Origin of Comets. In *The Motion, Evolution and*  
756 *Origin of Comets*, ed. G.A. Chebotarev. Springer Verlag, 329–334.

757 Schlichting, H.E., Sari, R., Yalinewich, A., 2014. Atmospheric Mass Loss during Planet Formation:  
758 The Importance of Planetesimal Impacts. *Icarus* 247, 81–94.

759 Schultz, L., Franke, L., 2004. Helium, Neon, and Argon in Meteorites: A data Collection. *Meteorit.*  
760 *Planet. Sci.* 39, 1889–1890.

761 Stern, S.A., et al., 2000. The Discovery of Argon in Comet C/1995 O1 (Hale Bopp). *Astrophys. J.*  
762 544, L169-L172.

- 763 Swindle, T.D., Kring, A., 2001. Implications of the noble gas budgets for the origin of water on  
764 Earth and Mars. *Lunar Planet. Sci. Conf.* # 3785.
- 765 Sugahara, H., and Mimura, K., 2014. Glycine Oligomerization up to Triglycine by Shock  
766 Experiments Simulating Comet Impacts. *Geochem. J.* 48, 51–62.
- 767 Takaoka, N., 1972. An Interpretation of General Anomalies of Xenon and the Isotopic Composition  
768 of Primitive Xenon. *Mass Spectrom.* 20, 287-302.
- 769 Tera, F., Papanastassiou, D.A., Wasserburg, G.J., 1974. Isotopic Evidence for a Terminal Lunar  
770 Cataclysm. *Earth Planet. Sci. Lett.* 22, 1–21.
- 771 Weaver, H.A., Feldman, P.D., Combi, M.R., Krasnopolsky, V. Lisse, C.M., Shemansky, D.E., 2002.  
772 A search for Argon and O<sub>VI</sub> in Three Comets Using the Far Ultraviolet Spectroscopic Explorer.  
773 *Astrophys. J.* 576, L95-L98.
- 774 Wetherill, G.W., 1980. Formation of the Terrestrial Planets. *Ann. Rev. Astron. Astrophys.* 18, 77-  
775 113.
- 776 Wong, M.H., et al., 2013. Isotopes of Nitrogen on Mars: Atmospheric Measurements by Curiosity's  
777 mass spectrometer. *Geophys. Res. Lett.* 40, 6033-6037.
- 778 Yokochi, R., Marboeuf, U., Quirico, E., Schmitt, B., 2012. Pressure Dependent Trace Gas Trapping  
779 in Amorphous Water Ice at 77 K: Implications for Determining Conditions of Comet  
780 Formation. *Icarus* 218, 760–770.

781

	lower	upper	mean	+/-	
<i>Water</i>			100		<b>1</b>
<i>Carbon</i>					
CO <sub>2</sub>	2.5	80	41	39	<b>2</b>
CO	1	30	16	15	<b>2</b>
CH <sub>4</sub>	0.6	1.5	1.05	0.45	<b>2</b>
C <sub>2</sub> H <sub>2</sub>	0.1	0.46	0.28	0.18	<b>2</b>
C <sub>2</sub> H <sub>6</sub>	0.4	10.5	5.45	5.05	<b>2</b>
others	0.4	2.4	1.40	1.00	<b>2</b>
ΣC			71	65	
<i>Nitrogen</i>					
NH <sub>3</sub>	0.3	1.5	0.90	0.60	<b>2</b>
HCN	0.1	0.6	0.35	0.25	<b>2</b>
N <sub>2</sub>			0.088	0.083	<b>3</b>
ΣN			1.43	1.02	
N <sub>2</sub> /ΣN			0.06	0.07	
<i>Argon</i>					
<sup>36</sup> Ar			1.20E-03	1.10E-03	<b>4</b>

782

783 **Table 1:** Coma composition. *1:* Species and elements are molar fractions normalized to water  
784 (=100). *2:* The range of C- and N-bearing species concentrations are for all comets analyzed so far  
785 (compiled from Bockelée-Morvan, 2011; Mumma and Charnley, 2011, Le Roy et al., 2015). *3:* The  
786 N<sub>2</sub> content is derived from the comet 67P measurement by Rubin et al. (2015), the good correlation  
787 between CO and N<sub>2</sub>, and the cometary CO content given above. *4:* Ar/H<sub>2</sub>O ratio from Balsiger et al.  
788 (2015).

789

790

791

	Coma		Bulk		
	mole/g	+/-	mole/g	+/-	
<sup>12</sup> C	0.012	0.011	0.037	0.028	
<sup>14</sup> N	0.00025	0.00018	0.0018	0.0010	794
H <sub>2</sub> O	0.017	0.0010	0.019	0.0010	
<sup>36</sup> Ar	2.07E-07	1.89E-07	2.07E-07	1.89E-07	795

796 **Table 2:** Cometary bulk composition. Abundances are computed with data from cometary  
797 composition (see text), Table 1 and refs. therein. The <sup>36</sup>Ar content is for 30% water ice.

798

799

800

	Atmosphere	Halliday, 2013 - HA				Marty, 2012 - MA				Dauphas &
		Mantle	atm.+mantle		Mantle	atm.+mantle		Morbidei, 2015		
	mol/g	mol/g	+/-	mol/g	+/-	mol/g	+/-	mol/g	+/-	DM, mol/g
<sup>12</sup> C	1.29E-06	4.00E-06	1.89E-06	5.29E-06	1.89E-06	6.38E-05	2.50E-05	6.51E-05	2.50E-05	5.60E-06
<sup>14</sup> N	5.98E-08	7.48E-09	4.71E-09	6.73E-08	8.97E-09	9.08E-08	4.60E-08	1.51E-07	4.60E-08	1.12E-07
H <sub>2</sub> O	1.48E-05	1.80E-05	6.00E-06	3.28E-05	6.00E-06	2.00E-04	9.60E-05	2.15E-04	9.60E-05	4.35E-05
<sup>36</sup> Ar	9.33E-13	3.03E-15	1.59E-15	9.36E-13	1.59E-15	7.83E-14	4.30E-14	1.01E-12	4.30E-14	9.29E-13

801

802 **Table 3:** Earth's volatile composition. Data are in mol/g for bulk Earth (mass =  $5.98 \times 10^{27}$  g).

803 "Atmosphere" refers to the atmosphere *sensu stricto*, the oceans and crustal and sedimentary rocks

804 (data are from Ozima and Podosek, 2002, Dauphas and Morbidelli, 2014, and refs. therein).

805 Uncertainties on the C and N contents of the "atmosphere" are ~20 %. Halliday (2013; HA)

806 considered the mantle sources of MORBs and of ocean basalt islands (note that the listed abundances

807 differ from those given by Halliday, 2013, in which some of the numbers could not be reproduced).

808 Marty (2012; MA) computed volatile element abundances from K-Ar systematics which predicts

809 that, for a K content of  $280 \pm 60$  ppm (1  $\sigma$ ; Arevalo et al 2009), half of radiogenic <sup>40</sup>Ar produced by

810 the decay of <sup>40</sup>K ( $T_{1/2} = 1.25$  Ga) over 4.5 Ga is still trapped in the mantle. The other volatile contents

811 are computed from <sup>40</sup>Ar/N/C/H<sub>2</sub>O ratio estimates for OIBs and MORBs. Dauphas and Morbidelli

812 (2014; DM) published recently estimates for volatile content of inner planets and other

813 cosmochemical reservoirs, which are intermediate between HA and MA abundances, although closer

814 to the former. HA and BM are assumed to represent two limiting cases for the Terrestrial inventory

815 of volatile elements in the silicate Earth+surface.

816

	Mars atm.	Carb. chondr.	Comets	
	mol/g	mol/g	mol/g	818
				819
$^{12}\text{C}$	$8.6 \cdot 10^{-10}$	$2.3 \cdot 10^{-3}$	$3.7 \cdot 10^{-2}$	820
$^{14}\text{N}$	$3.4 \cdot 10^{-11}$	$6.4 \cdot 10^{-5}$	$1.8 \cdot 10^{-3}$	
$^{36}\text{Ar}$	$9.1 \cdot 10^{-15}$	$3.9 \cdot 10^{-11}$	$2.1 \cdot 10^{-7}$	821
				822
C/N	25	36	21	
C/ $^{36}\text{Ar}$ , $10^4$	9.5	5,900	17.9	823
N/ $^{36}\text{Ar}$ , $10^3$	3.7	1,640	8.7	824
$^{20}\text{Ne}/^{22}\text{Ne}$	7 - 10	8.5 - 12.5	?	825
$\delta^{15}\text{N}$ ‰	572 ( $\pm 82$ )	-30 to + 150	+600 to +1,000	
$\delta\text{D}$ ‰	+5,500	-300 to +1,000	0 to 2,000	826
$F_{\text{Ne}}$ ‰/u	246	173	?	827
$F_{\text{Ar}}$ ‰/u	151	6	0	
$F_{\text{Kr}}$ ‰/u	$\pm 10$	10	0	828
$F_{\text{Xe}}$ ‰/u	33	3	0	829

830 **Table 4:** Volatile element composition of the Martian atmosphere (sensu lato, including estimates  
831 for surface reservoirs). Elemental abundance data are from Bogard et al. (2001), Dauphas and  
832 Morbidelli (2014), and refs. therein. Key elemental ratios and isotope data are also given, referenced  
833 in Bogard et al. (2001), Dauphas and Morbidelli (2014), Mahaffy et al. (2013), Atreya et al. (2013)  
834 and Wong et al. (2013). The  $\delta^{15}\text{N}$  values are given in parts per mil (‰) relative to terrestrial  
835 atmospheric nitrogen. The  $\delta\text{D}$  values are global estimates from Montmessin et al. (2005), given as  
836 deviations in ‰ relative to terrestrial ocean water. The  $F_X$  values (where X is a noble gas isotope  
837 ratio), represent deviations (in ‰ per atomic mass unit) from the solar composition (Dauphas and  
838 Morbidelli (2014). Note that Ar and Xe appear highly fractionated relative to Solar and compared to  
839 Kr, the latter being close to Solar. Ar, Kr and Xe are assumed to be isotopically solar in comets, as  
840 cometary ice should have trapped quantitatively these elements from the protosolar nebula. Neon is  
841 unlikely to have been trapped in comets, given the inferred formation temperature of these objects,  
842 and its abundance and isotopic composition cannot be inferred.



844 **Figure Caption**

845 **Fig. 1.** (a) Comparison of the abundance patterns of noble gases in the Sun ("Solar", yellow  
846 hexagons), in volatile-rich primitive meteorites ("CI", empty circles) and in the atmospheres of Earth  
847 (black-filled circles) and Mars (red squares). Note that the latter are depleted in xenon relative to  
848 krypton and meteorites by about a factor of 20, and that the Kr/Xe is close to the solar abundance  
849 (the "missing" Xe for Earth's atmosphere is represented by the blue area, see text). Modified after  
850 Porcelli and Ballentine (2002), Mars data from Dauphas and Morbidelli (2014). (b) Comparison of  
851 the Xe isotope compositions of meteoritic Xe (empty circles, "Q-Xe"), atmospheric Xe  
852 ("Atmosphere", black-filled circles), and Martian atmosphere Xe ("Mars-Xe", red squares),  
853 expressed in deviations in parts per mil (‰) relative to the solar composition (derived from solar  
854 wind measurements, yellow bar). In this format, the solar composition gives a flat spectrum at 0 ‰.  
855 The meteoritic composition is slightly different from Solar, whereas Martian and Terrestrial Xe are  
856 clearly fractionated (enriched in heavy isotopes) compared to solar, prohibiting direct derivation  
857 from the protosolar nebula and, by inference, from cometary ice (see text). Data from Ott (2014).

858 **Fig. 2:** Nitrogen vs. hydrogen isotope variations among solar system reservoirs (modified after  
859 Aléon, 2010, and Füri and Marty, 2015). The H and N isotopic ratios are normalized to the  
860 respective protosolar values. Fractionation trajectories are displayed for illustration. "Ion-molecule"  
861 is from Aléon (2010), representing isotope fractionation during ion molecule exchange. "Kinetic"  
862 illustrates the case of isotope fractionation proportional to the inverse square root of masses and is  
863 only one of the possibilities (others involve reduced masses, molecular masses instead of atomic  
864 masses etc.) Light blue dots: Giant planets; beige dots: inner planets and Titan; grey squares: bulk  
865 primitive meteorites; light green diamonds: comets.

866 **Fig. 3:**  $^{36}\text{Ar}/\text{H}_2\text{O}$  (a) and  $^{36}\text{Ar}/\text{N}$  (b) versus D/H mixing diagrams between cometary and chondritic  
867 (asteroidal) end-members. The mixing curves are constructed as  $[\text{X}/\text{Y}]_{\text{observed}} = \alpha \times [\text{X}/\text{Y}]_1 + (1-\alpha) \times$   
868  $[\text{X}/\text{Y}]_2$  for two end-members having cometary/chondritic elemental/isotopic compositions.



869 Coefficients  $\alpha$  are computed in each case using the end-member compositions (Tables 1 and 2).  
870 Terrestrial reservoir compositions from Table 3: HA, DM and MA are the bulk Earth estimates from  
871 Halliday (2013), Dauphas and Morbidelli (2014) and Marty (2012), respectively. Dotted lines  
872 indicate the percentage of cometary water (a) and of cometary nitrogen (b), respectively, on Earth.

873 **Fig. 4:** D/H versus  $^{36}\text{Ar}/\text{C}$  mixing diagram between cometary and chondritic (asteroidal) end-  
874 members. HA, DM and MA are the bulk Earth estimates from Halliday (2013), Dauphas and  
875 Morbidelli (2014) and Marty (2012), respectively. *a*: Dotted lines indicate the percentage of  
876 Terrestrial carbon of cometary origin. *b*: Dotted lines indicate the percentage of cometary  $^{36}\text{Ar}$  on  
877 Earth.

878 **Fig. 5:** Abundances of C, N,  $\text{H}_2\text{O}$  and  $^{36}\text{Ar}$  in the atmosphere *sensu largo* (air+oceans+sediments),  
879 normalized to Chondritic (data from Tables 2 and 3). For comparison bulk Earth inventories from  
880 Table 4 are also represented. *5a*: Effect of addition of a late veneer (0.3 % of the Terrestrial mass)  
881 made of 100 % comet. The  $^{36}\text{Ar}$  inventory of the atmosphere (the main reservoir of noble gases) is  
882 overabundant by several orders of magnitude, and major volatiles are also dominated by cometary  
883 material. *5b*: same as *3a* but for a tiny contribution of cometary material in the late Veener,  
884 arbitrarily chosen as 0.2 % to fit the Terrestrial abundances. *5c*: Effect of contribution of a Terrestrial  
885 Late Heavy Bombardment ( $2 \times 10^{23}$  g) made of 100 % comet. Given the uncertainties, the  $^{36}\text{Ar}$   
886 content of the atmosphere can be matched, but the major volatiles at the Earth's surface are  
887 dominated by a cometary component. *5d*: A~10% cometary contribution in the TLHB fits well the  
888  $^{36}\text{Ar}$  inventory of the atmosphere, without impacting the isotope compositions of C, N and H. *5e*:  
889 Effect of addition of a continuous IDP flux since 3.5 Ga ago. This flux has no impact on the  
890 Terrestrial inventory of H, C, N and  $^{36}\text{Ar}$ .

891 **Fig. 6:** Elemental composition of the Martian atmosphere, compared to Earth's atmosphere and  
892 comets. Data sources: Pepin, 1991; Bogard et al., 2001; Dauphas and Morbidelli (2014). Water is not

893 represented here since its Martian inventory is unknown. The effects of a Martian late veneer (M-  
894 LV), a Martian Late Heavy Bombardment (M-LHB) and continuous IDP flux are also represented.

895 **Fig. 7:** N isotope vs.  $^{36}\text{Ar}/\text{N}$  ratio mixing diagram between carbonaceous chondrite (CCs) and comet  
896 end-members. The dotted curves represent mixing trajectories between Comet and CCs on one hand,  
897 and between MSL measured Martian atmospheric composition on another hand. between Viking and  
898 Martian meteorite data are from Bogard et al. (2001) and refs. therein, and Chennaoui-Aoudjehane et  
899 al. (2012). MSL data are from Wong et al. (2013) and Mahaffy et al. (2013).

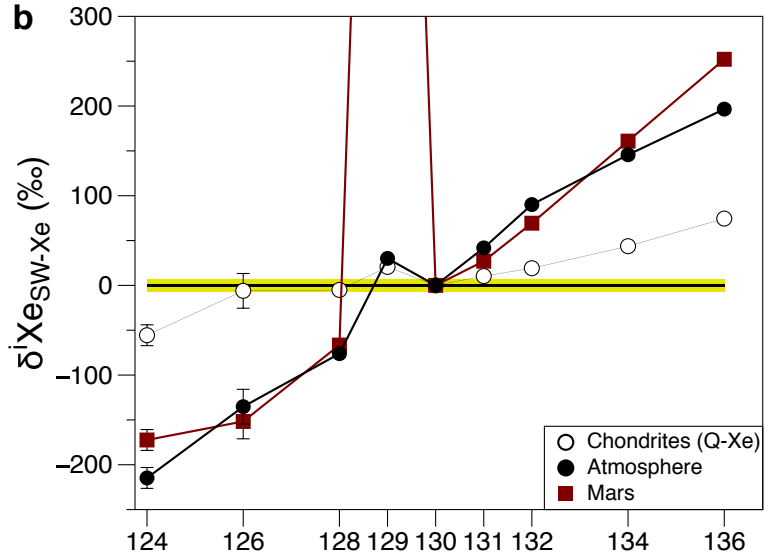
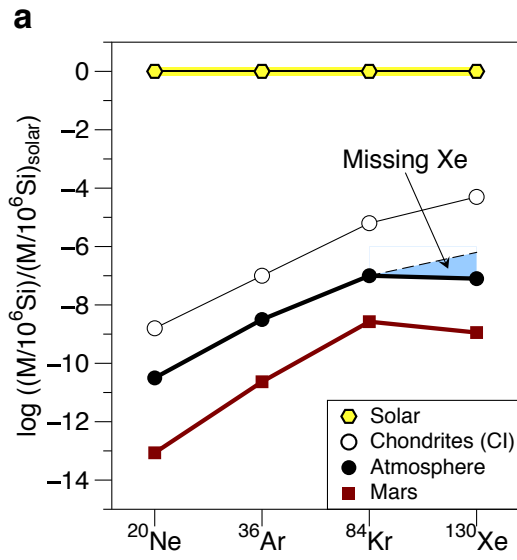
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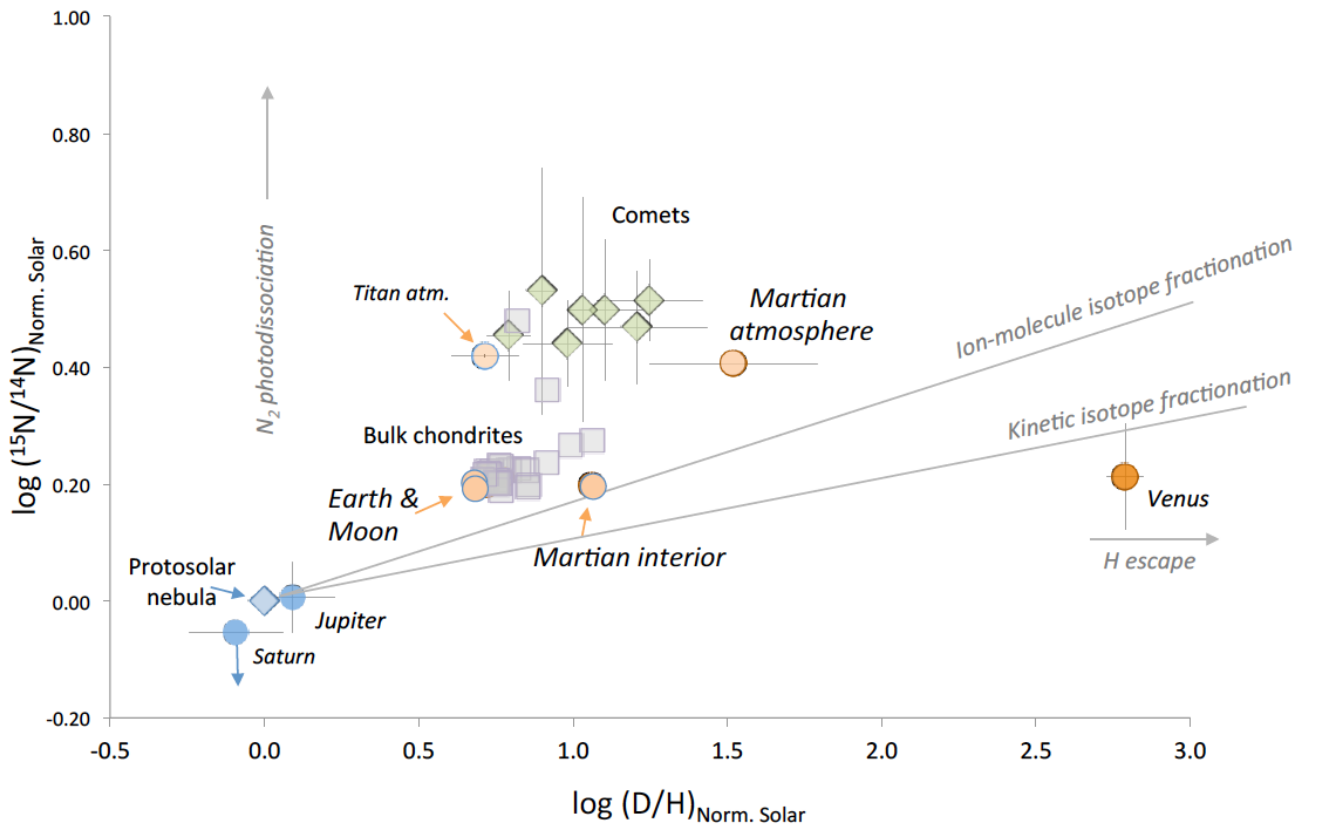
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**Fig. 1**

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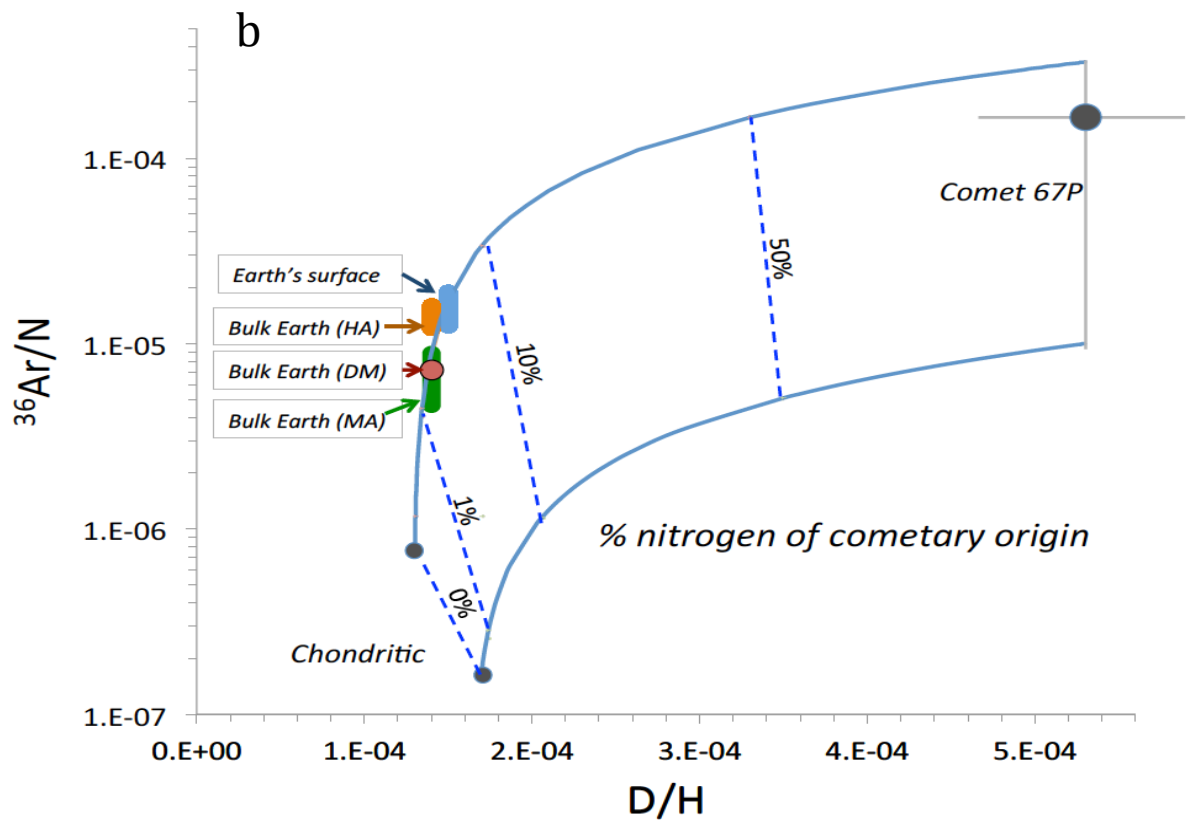
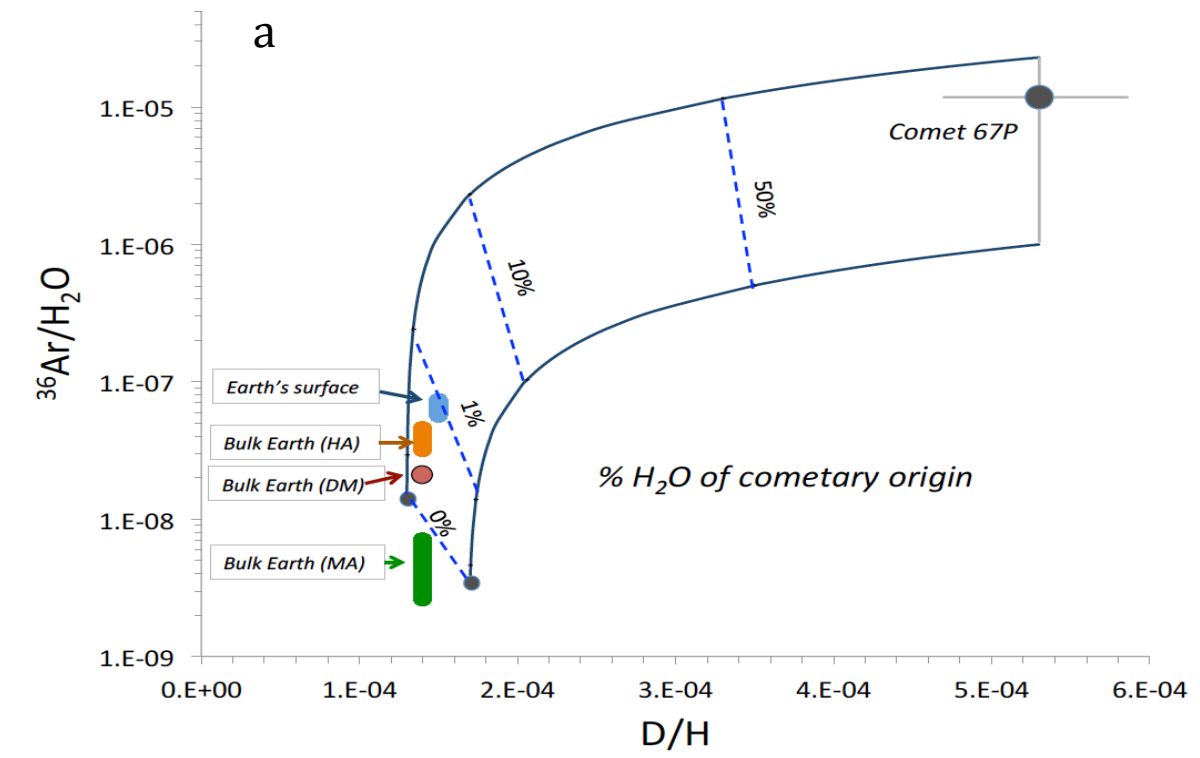
911 **Fig. 2**

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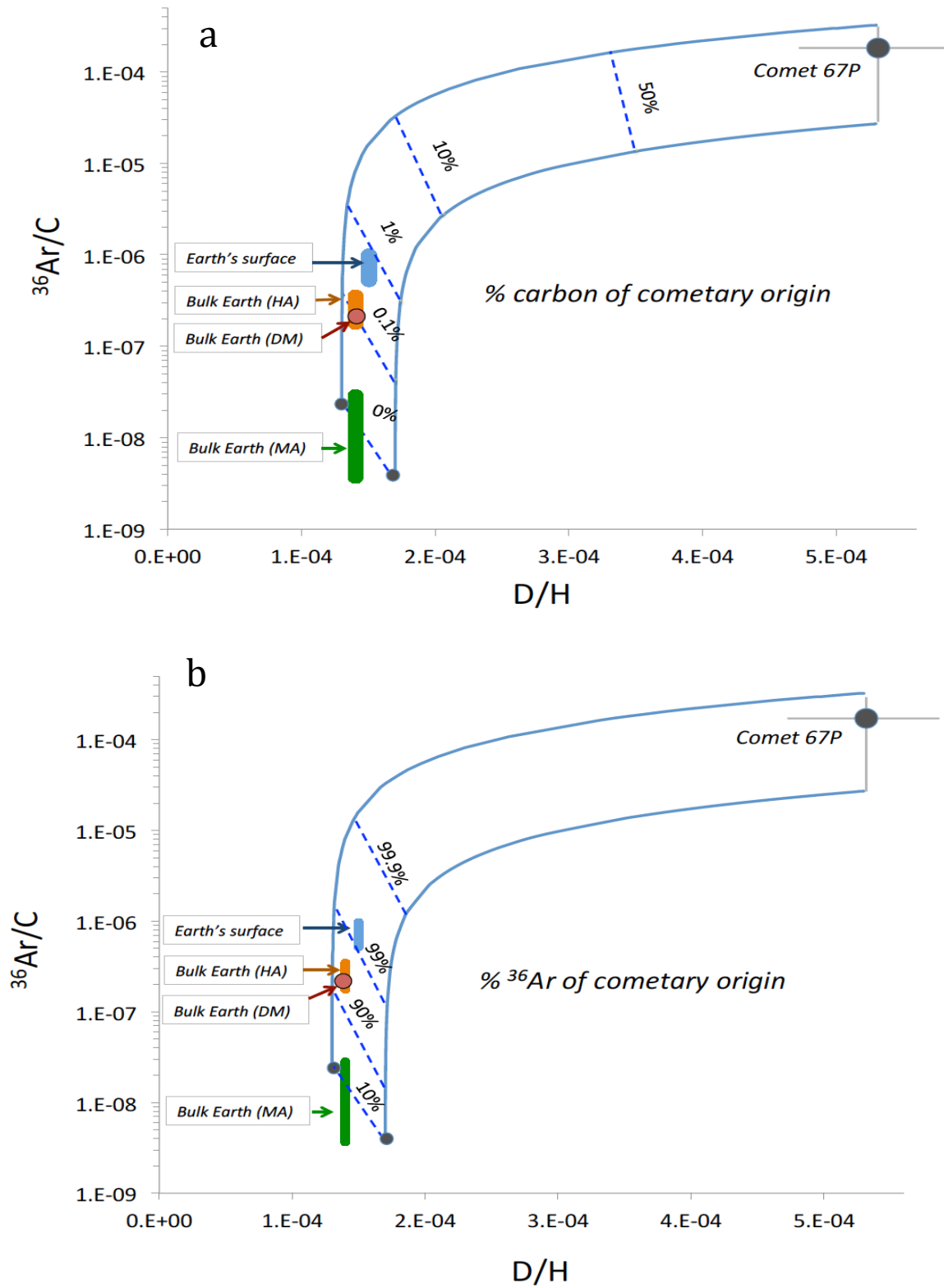
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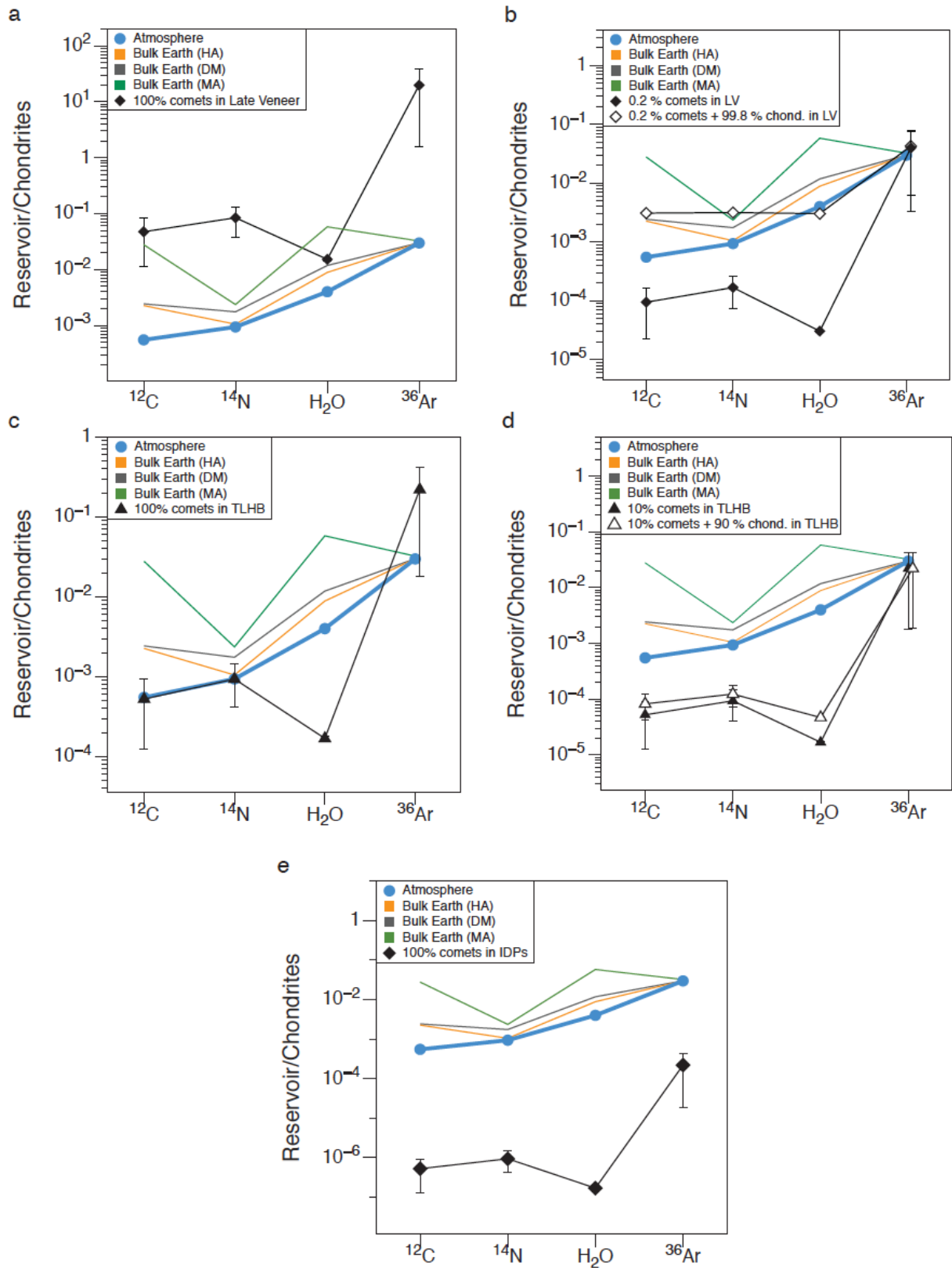
917 **Fig. 3**



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921 **Fig. 4**

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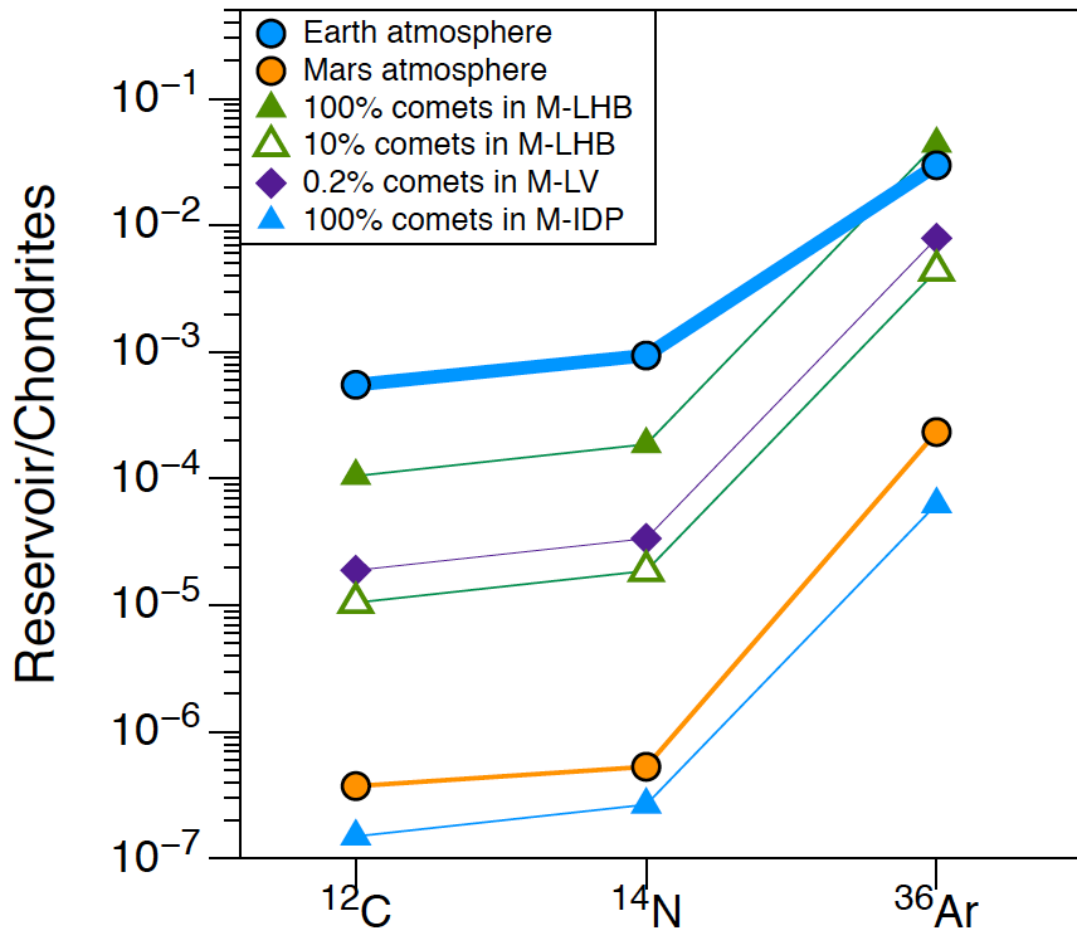


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**Fig. 5**

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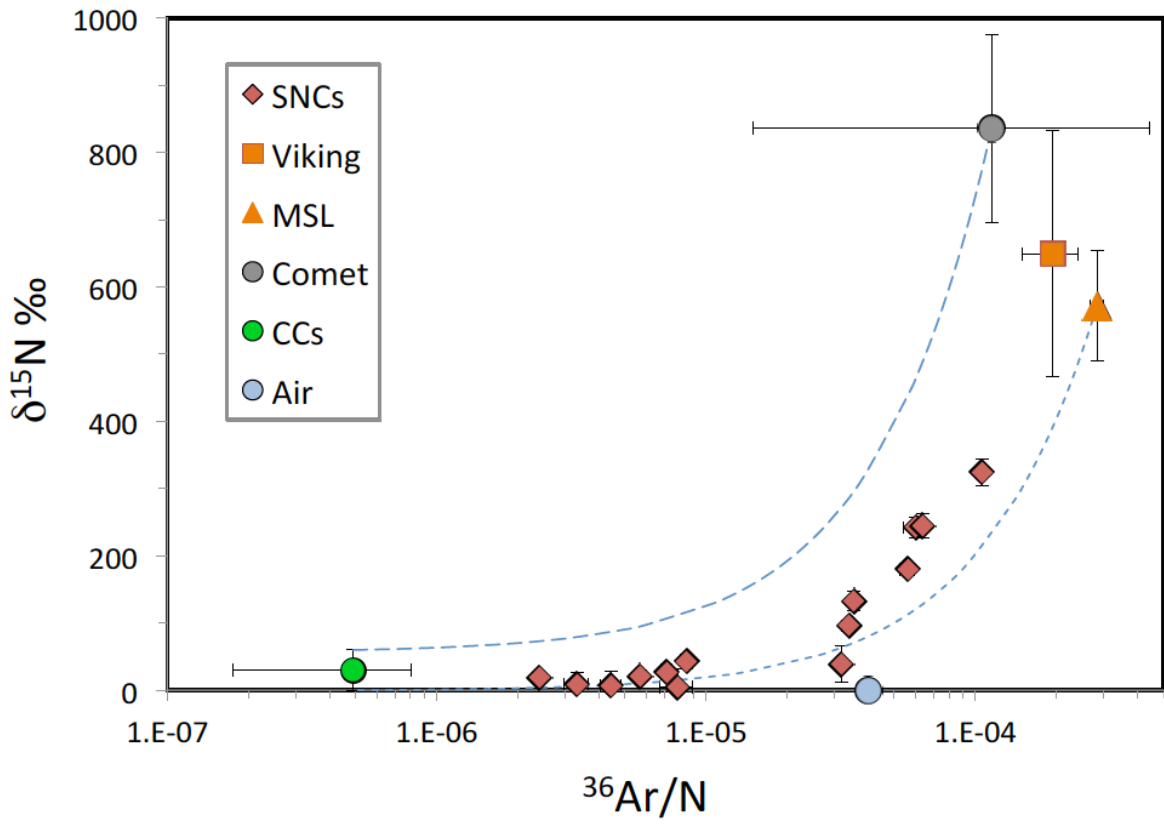
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930 **Fig. 6**

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934 **Fig. 7**