

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

Bernard Marty, Guillaume Avice, Yuji Sano, Kathrin Altwegg, Hans Balsiger, Myrtha Hässig, Alessandro Morbidelli, Olivier Mousis, Martin Rubin

▶ To cite this version:

Bernard Marty, Guillaume Avice, Yuji Sano, Kathrin Altwegg, Hans Balsiger, et al.. Origins of volatile elements (H, C, N, noble gases) on Earth and Mars in light of recent results from the ROSETTA cometary mission. Earth and Planetary Science Letters, 2016, 10.1016/j.epsl.2016.02.031. hal-01345988

HAL Id: hal-01345988 https://hal.science/hal-01345988

Submitted on 20 Jul 2016

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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	
4	Bernard Marty ^{1*} , Guillaume Avice ¹ , Yuji Sano ² , Kathrin Altwegg ³ , Hans Balsiger ³ , Myrtha
5	Hässig ³ , Alessandro Morbidelli ⁴ , Olivier Mousis ⁵ , Martin Rubin ³
6	
7	1: Centre de Recherches Pétrographiques et Géochimiques, CRPG-CNRS, Université de Lorraine,
8	UMR 7358, 15 rue Notre Dame des Pauvres, BP 20, 54501 Vandoeuvre lès Nancy, France.
9	
10	2: Ocean and Atmosphere Research Institute, The University of Tokyo, 5-1-5, Kashiwanoha,
11	Kashiwa-shi, Chiba 277-8564 Japan
12	
13	3: Physikalisches Institut, University of Bern, Sidlerstr. 5, CH-3012 Bern, Switzerland.
14	
15	4: Laboratoire Lagrange, Université Côte d'Azur, CNRS, Observatoire de la Côte d'Azur, Boulevard
16	de l'Observatoire, BP 4229, 06304 Nice Cedex 4, France
17	
18	5: Aix Marseille Université, CNRS, LAM (Laboratoire d'Astrophysique de Marseille) UMR 7326,
19	13388, Marseille, France.
20	
21	* Corresponding author: bmarty@crpg.cnrs-nancy.fr
22	
23	

24 Abstract

Recent measurements of the volatile composition of the coma of Comet 67P/Churyumov-25 Gerasimenko (hereafter 67P) allow constraints to be set on the origin of volatile elements (water, 26 carbon, nitrogen, noble gases) in inner planets' atmospheres. Analyses by the ROSINA mass 27 spectrometry system onboard the Rosetta spacecraft indicate that 67P ice has a D/H ratio three times 28 that of the ocean value (Altwegg et al., 2015) and contains significant amounts of N₂, CO, CO₂, and 29 importantly, argon (Balsiger et al., 2015). Here we establish a model of cometary composition based 30 on literature data and the ROSINA measurements. From mass balance calculations, and provided 31 that 67P is representative of the cometary ice reservoir, we conclude that the contribution of 32 cometary volatiles to the Earth's inventory was minor for water ($\leq 1\%$), carbon ($\leq 1\%$), and nitrogen 33 species (a few % at most). However, cometary contributions to the terrestrial atmosphere may have 34 been significant for the noble gases. They could have taken place towards the end of the main 35 building stages of the Earth, after the Moon-forming impact and during either a late veneer episode 36 37 or, more probably, the Terrestrial Late Heavy Bombardment around 4.0-3.8 billion years (Ga) ago. Contributions from the outer solar system via cometary bodies could account for the dichotomy of 38 39 the noble gas isotope compositions, in particular xenon, between the mantle and the atmosphere. A mass balance based on ³⁶Ar and organics suggests that the amount of prebiotic material delivered by 40 comets could have been quite considerable – equivalent to the present-day mass of the biosphere. On 41 Mars, several of the isotopic signatures of surface volatiles (notably the high D/H ratios) are clearly 42 indicative of atmospheric escape processes. Nevertheless, we suggest that cometary contributions 43 after the major atmospheric escape events, e.g., during a Martian Late Heavy Bombardment towards 44 the end of the Noachian era, could account for the Martian elemental C/N/³⁶Ar ratios, solar-like 45 krypton isotope composition and high ¹⁵N/¹⁴N ratios. Taken together, these observations are 46 consistent with the volatiles of Earth and Mars being trapped initially from the nebular gas and local 47 accreting material, then progressively added to by contributions from wet bodies from increasing 48 heliocentric distances. Overall, no unified scenario can account for all of the characteristics of the 49

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

According to cosmochemical constraints and simulations, the inner planets grew first "dry", and

52 **1. Introduction**

53 54

water and atmophile elements were contributed later on by volatile-rich objects originating from 55 larger heliocentric distances (Morbidelli et al., 2000; Raymond et al., 2004; Albarède et al., 2013; 56 Marty, 2012). A cometary origin for the Terrestrial oceans, the atmosphere and the organics is often 57 advocated (Oro, 1961; Anders and Owen, 1977; Safronov, 1972) because (i) comets are volatile-rich 58 as they contain abundant organics and ices (30-50 wt. % H₂O), and (ii) their high eccentricities and 59 hyperbolic trajectories increase their probability to encounter inner solar system bodies. Other 60 potential sources of water are "wet" asteroids. Meteorites are generally dry, although some of them, 61 the carbonaceous chondrite clan, can contain up to 15 wt. % equivalent H₂O as hydrated phases. 62 Because these phases are remnant of water-rock interactions on asteroids, the original water content 63 64 could have been significantly higher, possibly matching those of comets. This would argue in favor of a continuum between meteoritic and cometary compositions in the past. The Terrestrial oceans 65 $(1.5 \times 10^{24} \text{ g})$ correspond to 0.025 % of the Earth's mass. Taking into account water in the deep Earth

 $(1.5 \times 10^{24} \text{ g})$ correspond to 0.025 % of the Earth's mass. Taking into account water in the deep Earth may raise the Terrestrial H₂O inventory to a maximum of 0.2 wt. % (Marty, 2012). Assuming conservation of volatile elements during impacts, that is, no loss of volatiles to space (an assumption discussed later on), Terrestrial water could have been supplied by a few wt. per mil to a few wt. percent of cometary, or asteroidal, material to a dry proto-Earth, leaving the bulk chemical composition of Earth little affected.

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

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

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

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

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

comets have ${}^{15}N/{}^{14}N$ ratios about two times the Terrestrial and bulk chondritic values (Fig. 2). One possible caveat is that only HCN, CN, and NH_2^+ could be measured at distance by spectroscopy (there is no in-situ measurement on a comet), and it is not clear if these nitrogen species are representative of bulk cometary N.

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

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

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

several high temperature phases reminiscent of chondritic material. These are calcium-aluminium 152 rich inclusions, chondrules and refractory olivines. Stable isotope compositions of these phases 153 indicate an inner solar system origin for this material (Brownlee, 2006). From mass balance, silicate 154 + metal (Si, Mg, Fe) grains make about 25-30 wt. % (Jessberger et al., 1988). Refractory organics 155 constitute a significant fraction of C and, to a lesser extent, of N and H, and must be taken into 156 account in the bulk composition of cometary matter (Greenberg, 1998). This is confirmed by a 157 refractory organics/silicate+metal ratio close to 1 for dust emitted by comet Halley (Kissel and 158 Krueger, 1987). Therefore, organic refractory particles (the so-called CHON grains, Jessberger et al., 159 1988) could make another 25-30 wt. %, and non-refractory carbon-bearing species could contribute 160 about 4-8 wt. % (Greenberg, 1998). The proportion of ice amounts for 30-50 wt. %. The composition 161 of comae (Table 1) gives insight into the ice composition (~ 80 wt. % H₂O with CO, CO₂, CH₃OH, 162 CH₄, H₂S, and N-compounds including CN, HCN, NH₃ and N; Bockelée-Morvan, 2011; Hässig et 163 164 al., 2015; Rubin et al., 2015).

Noble gases are able to set stringent constraints on the origin of planetary volatiles on one hand, 165 and on processes and conditions of comet formation on another hand. Unfortunately the abundances 166 of noble gases in comets are essentially unknown as these elements are extremely difficult to detect 167 by spectroscopy. Stern et al. (2000) proposed an Ar/O ratio of 1.8±1.0 x 10⁻⁴ for Comet Hale Bopp, 168 lower than the solar value of 46 x 10^{-4} (Weaver et al., 2002, and refs. therein), but this estimate has 169 170 not been confirmed. Weaver et al. (2002) suggested that the cometaryAr/O ratios are lower than 42 x 10⁻⁴, based on three comet observations. The only reliable set of measurements are those done on 67P 171 coma using the ROSINA mass spectrometer which directly the 67P coma composition (Balsiger et 172 al., 2015). They indicate a ³⁶Ar/H₂O varying between 0.1 x 10⁻⁵ and 2.3 x 10⁻⁵ during the 3 days 173 measurement period. Considering that Ar/O ~1.3 Ar/H₂O (Weaver et al., 2002), and taking into 174 account a solar isotope composition for argon (40 Ar ~ 0, 38 Ar/ 36 Ar = 0.183), the corresponding Ar/O 175 range of 67P is $0.01-0.35 \times 10^{-4}$, thus lower than the upper limits given above, and 2-3 orders of 176 magnitude lower than the solar ratio of 46 x 10⁻⁴. It is worth mentioning that even if noble gases are 177

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

182 2.1.2. Isotopes

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

199 2.2 Carbonaceous chondrites

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

respective mean chondritic abundances of C, N, H₂O and ³⁶Ar are, in mol/g: $2.3\pm1.2 \times 10^{-3}$, $6.4\pm2.5 \times 10^{-5}$, $3.7\pm1.0 \times 10^{-3}$ and $3.1\pm1.6 \times 10^{-11}$, respectively.

204 2.3 Earth

The inventory of volatile elements at the Earth's surface (the atmosphere, the oceans and the crust) 205 is reasonably well known. The problem is to estimate the amount of volatiles in the mantle, since 206 magmas tend to degas readily upon eruption, and the inferred source compositions are model-207 dependent. Recent estimates of the bulk Earth (mantle plus surface) volatile inventories have been 208 given by Marty (2012), Halliday (2013) and Dauphas and Morbidelli (2014). We adopt here two 209 limiting cases. The lower limit is based on the reconstruction of the initial volatile inventory of the 210 mantle regions sampled by volcanism. The initial contents of water, C, N and noble gases in the 211 mantle source of mid-ocean ridge basalts (MORB; volumetrically the main source of lavas at the 212 213 Earth's surface) is derived from a combination of lava fluxes and calibration to relevant tracers like ³He or refractory elements like Ce, Nb. Halliday (2013) considered also the source of Ocean Island 214 basalts (another important source of volcanism thought to tap deep regions of the mantle), ("HA" in 215 Figs. 3 and 4). Dauphas and Morbidelli (2014; "DM") obtained an inventory comparable to the one 216 of Halliday (2013) from global calibration of volatiles to refractory (Ce, Nb) elements, and obtained 217 a total bulk Earth water content of about 3 ocean masses (M_{Ocean} equivalent to 230 ppm H₂O for bulk 218 Earth). The isotopic compositions of helium, neon, argon and xenon suggest that deep mantle regions 219 could be richer in volatiles than the convective mantle sampled by mid-ocean ridges. K-Ar 220 systematics indicate that about half of radiogenic ⁴⁰Ar produced in Earth over 4.5 Ga is still trapped 221 in the solid Earth, the rest having been degassed into the atmosphere (Allègre et al., 1996). 222 Calibrating volatile elements to ⁴⁰Ar trapped in the mantle led Marty (2012) to propose a bulk mantle 223 ("MA") higher than the above estimates, corresponding to 4-10 ocean masses. This approach does 224 not rely on models of the structure and the composition of mantle domains. However, it assumes a 225 chondritic composition for Terrestrial refractory elements. This is because the potassium content of 226

the Earth (Arevalo et al., 2009) is calibrated against refractory uranium as potassium is semi-volatile and its abundance cannot be retrieved from meteoritic analogs. A chondritic Earth composition for refractory elements has been recently questioned on the basis of sub-chondritic Terrestrial Nd isotope ratios, with the possibility that up to half of U, and therefore K, could have been stripped off by impacts on a differentiated Earth (e.g., Jellinek and Jackson, 2015; and refs. therein). This would reduce the ⁴⁰Ar inventory and therefore allow much lower volatile contents. For this reason, we 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?*

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

For noble gases, the Ar measurement of Balsiger et al. (2015) is the only available set of data, but we propose below that the range of observed values is representative of the coma composition. Fractionation of a minor, low temperature species/element like argon relative to H_2O can range over 1-2 order(s) of magnitude, depending on its sublimation temperature relative to that of H_2O ice. Marboeuf and Schmitt (2014) modeled fractional degassing of cometary volatiles as a function of the distance to the perihelion, under a range of different assumptions concerning the thermal inertia of a comet, the nature of ice, and the abundance and distribution of the different volatile species. Argon

was not considered in their study, so we take as a proxy CO which has a comparable 251 condensation/sublimation temperature. Results of their modeling indicate that, at a distance between 252 3 and 4 AU from the perihelion, the CO/H₂O ratio of the coma is comparable to that of the bulk 253 comet. Argon measurements by the ROSINA mass spectrometer were done on October 19, 20, 22, 254 and 23, 2014 when Comet 67P was at ~3.1 AU from the Sun, thus possibly minimizing fractionation 255 of minor species like Ar relative to H₂O. The 67P ³⁶Ar/H₂O ratio of 0.1-2.3 x 10⁻⁵ is also comparable 256 to, although lower than, ratios predicted from modeling of ice trapping experiment data (2-40 x 10⁻⁵ 257 in the 30-45 K range according to Dauphas, 2003; 8-75 x 10⁻⁵ according to Marty and Meibom, 2007, 258 based on experimental data from Notesco and Bar-Nun, 2005). Models and experiments of noble gas 259 trapping into cometary ice indicate that the main controlling factors on the abundance of trapped 260 noble gases are the temperature and the partial pressures of gases (Bar-Nun et al., 1985; Yokochi et 261 al., 2012), so that other parameters of comet formation being equal, we assume that the Ar content of 262 cometary matter is represented by 67P data. Although the above assumptions may constitute the 263 main weak point of the present approach, we note that uncertainty range covers one order of 264 magnitude of the stated values (the ³⁶Ar/H₂O ratio) whereas the present conclusions here are based on 265 variations of key parameters over several orders of magnitude. 266

267 3.2. Impact driven atmospheric loss

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

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

294 3.3. Origin of major volatile species on Earth

The Ar content of cometary material inferred from the analysis of argon in 67P coma is 3-4 orders of magnitude higher than the one of chondritic material, which makes Ar, and by inference other heavy noble gases, a key tracer of cometary contribution to Earth. Together with the D/H ratio, the ratio between argon and H_2O , C and N permits to establish firm constraints on the contribution of 67P-like material to Terrestrial volatiles. Swindle and Kring (2001) considered the ratio between ³⁶Ar and H_2O in comets (they took the Hale Bopp's ³⁶Ar/O ratio from Stern et al., 2000, which has been

questioned since then) to infer an extremely low contribution of cometary material to the surfaces of 301 Earth and Mars. Dauphas (2003) noted that the low Xe/H₂O ratio of the Earth compared to other 302 cosmochemical end-members could set stringent constraints on the maximum amount of cometary 303 water on Earth. Since then, it has been proposed that the low terrestrial Xe/H₂O ratio could be 304 secondary (Pujol et al., 2011), making the argument less constraining. Figs. 3 and 4 represent mixing 305 curves between chondritic and cometary end-members using the ³⁶Ar/X (where X represents water, 306 nitrogen or carbon) ratio versus the D/H ratio. In fact the ³⁶Ar concentration is more sensitive than 307 the D/H ratio alone, because contribution of 67P-like material can strongly impact the atmospheric 308 inventory of argon. For water, a cometary contribution of the order of 1% or less is allowed 309 depending on the bulk silicate Earth + surface composition (Fig. 3a), confirming that Terrestrial 310 311 water is mostly non-cometary. A comparable conclusion arises for nitrogen (Fig. 3b), although a larger cometary contribution up to a few percent is allowed, due to the depletion of N in Earth 312 313 (Marty, 2012). Nitrogen isotopes may permit to get independent constraints because spectroscopic measurements on comets indicate that the measured N-bearing species, CN, HCN and NH₂ (the latter 314 presumably from NH₃) are all enriched by a factor of 2 in ¹⁵N relative to ¹⁴N (e.g., Füri and Marty, 315 2015, for a review). However, other N species like N₂ (Rubin et al., 2015) and refractory organics are 316 present in comets with unknown N isotope composition, preventing to establish an isotope budget for 317 the cometary reservoir. 318

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

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

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

already proposed by Anders and Owen (1977) and Owen and Bar-Nun (1995) based on the noble gas 326 abundance pattern of the atmosphere, and by Marty and Meibom (2007) from mass balance 327 considerations. For the bulk silicate Earth inventory, the conclusion depends on the adopted 328 composition. For the HA and DM inventories, a major cometary origin for argon is clearly possible 329 (Fig. 4b). The MA inventory does not require contribution of cometary noble gases to the bulk Earth 330 (Fig. 4b). In this model, noble gases are mostly in the atmosphere, and major volatiles (H₂O, C) are 331 in the mantle, the sum of which being consistent with the addition of ~ 2 wt. % of carbonaceous 332 chondrite type material. 333

334 3.5. Potential cometary contribution during the major bombardment periods

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

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

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

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

4- The Terrestrial late heavy bombardment (TLHB) is an extrapolation of the late heavy 360 bombardment thought to have occurred on the Moon from the size-age distribution of lunar craters 361 (Tera et al., 1974). Estimates of the mass contribution to Earth during the TLHB, based on the Lunar 362 cratering record, range from 2.2 x 10²³ g (Hartmann et al., 2002) down to 4 x 10²² g (assuming that 363 the TLHB started at the time of formation of Nectaris basin; Morbidelli et al., 2012). From a 364 modeling approach, Levison et al. (2001) proposed a mass contribution of 8 x 10^{22} g. Gomes et al. 365 (2005) estimated a TLHB of 4 $x10^{23}$ g, about half of which being cometary. The newest version of 366 the Nice model, however, reduces the mass flux to the Earth to about $4 \ge 10^{22}$ g of asteroidal material 367 (Bottke et al., 2012) and 2-4 x 10²² g of cometary material (depending on the dynamical state of the 368 trans-Neptunian disk before the dynamical instability). For the calculations presented here, a 369 conservative value of 2.0 x 10^{23} g is adopted. Marty and Meibom (2007) concluded that less than 1 % 370 comets were present in the TLHB, the rest being asteroidal material, and proposed that atmospheric 371 noble gases could constitute the only remaining evidence for the TLHB. Their mass balance was 372 based on noble gas cometary concentration from ice trapping experiments, which are higher than the 373 one constrained by Ar in 67P. With the ROSINA ³⁶Ar measurement, a 100% cometary TLHB would 374 supply too much ³⁶Ar to the atmosphere (Fig. 5c). It would also supply most major volatiles at the 375

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

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

From isotope geochemistry considerations, several distinct cosmochemical sources contributednoble gases to the growing Earth.

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

395 (ii) The isotopic compositions of H, N and mantle Kr isotopes are consistent with a chondritic396 source.

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

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

Given the possible cometary origin of atmospheric noble gases, we speculate that this exotic Xe 409 component could have been carried out from the outer solar system to its inner region by icy bodies. 410 The dichotomy between mantle chondritic Xe and surface Xe would then be a record of Terrestrial 411 412 growth, with the Proto-Earth being built from chondritic-like material, and its surface having been subsequently contributed by cometary bodies. In order to supply all atmospheric ³⁶Ar (5.55 x 10¹⁵ 413 moles, Ozima and Podosek, 2002), a cometary contribution between 3 x 10^{21} and 6.5 x 10^{23} g would 414 have been necessary (computed with a ³⁶Ar cometary concentration of 2.1±1.9 x 10⁻⁷ mol/g, and a 415 cometary density of 0.5 from the 67P measurements). This is in great agreement with the most recent 416 417 estimates of the cometary flux to the Earth during the TLHB. Thus, there is no "missing comet bombardment" unlike the earlier conclusions of Marty and Meibom (2007) based on an higher ³⁶Ar 418 content of comets. The impact of a single cometary body with a radius of 100-300 km, or of a limited 419 number of smaller bodies, could have sufficient to supply all atmospheric argon. Therefore, it may be 420 possible that the supply of atmospheric volatiles to the Terrestrial planets was a stochastic process 421 involving a small population of objects, which might have resulted in an heterogeneous distribution 422 of outer solar system isotopic signatures. In this respect, the high abundance of ³⁶Ar in the 423

424 atmosphere of Venus could effectively be the result of random contribution of cometary material ton425 inner planets.

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

Peptide synthesis from amino-acids appears a necessary step for the development of prebiotic 427 material on Earth. Although a number of possible scenarios invoking catalytic reactions in specific 428 Terrestrial environments have been advanced, it has also been proposed that impacts could have 429 favored peptide synthesis from ET amino-acids (Blank et al., 2001). Sugahara and Mimura (2014) 430 simulated comet impacts by shock experiments at low temperature in the range 5-26 GPa and found 431 that linear peptide synthesis up to tripeptide forms could be achieved only with initially low 432 temperature. As formation of linear peptide appears a key process for further elongation of peptide 433 chains, these authors argued that comet impacts might have played a key role in the formation of 434 prebiotic material on Earth. An upper limit for the total delivery of potential prebiotic material to 435 Earth by comets can be set by considering that all atmospheric ³⁶Ar was delivered by icy bodies to 436 the Earth's surface. Carbonaceous chondrites contain about 80 different amino-acids (Ehrenfreund 437 and Charnley, 2000), with their total concentration amounting for 250 ppm (e.g., Martins et al., 438 2007). Their concentration in cometary matter is unknown. Studies of Stardust cometary grains 439 suggest similarities with stratospheric IDPs and carbonaceous chondrites (Brownlee et al., 2006). 440 Thus, for the purpose of illustration, we consider that the carbonaceous chondrite concentration is 441 representative of cometary matter. The mass of cometary material having the ³⁶Ar content of 67P 442 $(2.1\pm1.9 \text{ x } 10^{-7} \text{ mol/g})$ that would have delivered atmospheric ³⁶Ar (5.55 x $10^{15} \text{ moles})$ is 0.2-5 x 10^{22} 443 g, leading to the delivery of $0.6-13 \times 10^{18}$ g of amino acid-rich material. This amount is comparable 444 to the present-day mass of the biosphere ($\sim 2 \times 10^{18}$ g). With the present-day mass of the oceans, 445 comets could have delivered up to 10-40 ppm prebiotic material to seawater. Thus depending on the 446 efficiency of survival and of peptide synthesis upon impact, comets might have contributed non-447 negligible prebiotic material during the TLHB. 448

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

The atmospheric signatures have been interpreted as resulting from isotope fractionation during 461 atmospheric escape processes. Possibilities include solar wind-induced photochemical reactions 462 producing electrons able to dissociate N₂ for nitrogen (Mc Elroy et al., 1976), and sputtering for the 463 noble gases (Jakosky et al., 1994). Chassefière and Leblanc (2004) reviewed potential escape 464 mechanisms that might have affected the atmosphere of Mars and concluded that (i) not a single 465 466 process can account for the observations; and (ii) non-thermal processes are required and therefore might have affected different atoms/species at variable levels independently of their masses. 467 Atmospheric loss is attested by morphological evidence on Mars indicating past water flows (Carr 468 and Head, 2003), and major escape processes might have taken towards the end of the Noachian 469 period 4.0-3.7 Ga ago. Thus escape-related fractionation of Martian volatiles is likely to have played 470 a key role in fractionating elemental abundances and isotopic compositions. Nevertheless, we 471 suggest here that possible source effects, namely cometary contributions, should be also considered, 472 especially after the major escape events that resulted in a tenuous atmosphere on Mars. 473

Several key observations are not entirely consistent with atmospheric escape as a cause of isotopic 474 enrichments. (i) The noble gas elemental abundance of the Martian atmosphere and the C/N ratio 475 (Pepin, 1991) are comparable to those of Venus and Earth (for which similar escape fractionations 476 are unlikely). (ii) The krypton isotopic composition of the Martian atmosphere is close to the solar 477 composition (Bogard et al., 2001, and refs. therein), contrary to those of Ne, Ar and Xe (Table 4). 478 Because the mass of Kr is intermediate betwen those of Ne, Ar and Xe, this difference points to other 479 processes than escape-related fractionation. We note that the Martian Ne isotopic composition is 480 within the range of chondritic values, e.g., the so-called Ne-A (planetary) component of 481 carbonaceous chondrites. Neon is not expected to be trapped in comets, so that Martian atmospheric 482 Ne could have been sourced by an another cosmochemical reservoir. The high ³⁸Ar/³⁶Ar ratio (0.238) 483 ± 0.005; Atreya et al., 2013) is indeed a good diagnostic of escape-related fractionation, but cosmic-484 ray production of noble gas isotopes (which also increases this ratio) could have been sigificant for 485 486 the tenuous Martian atmosphere. Such effects need to be assessed. The Xe isotope fractionation could have arisen from a Xe-specific non-thermal escape process, like the one proposed for 487 Terrestrial atmospheric Xe (Pujol et al., 2011). (iv) The isotopes of C, O, S in the Martian surface 488 and crust are little fractionated. CO₂ is enriched in ¹³C relative to Terrestrial ($\delta^{13}C = 46 \pm 4$ ‰; 489 Mahaffy et al., 2013) but to a much lesser extent than ¹⁵N in nitrogen ($\delta^{15}N = 572\pm82$ %, Wong et al., 490 491 2013). However this argument is not carved in stone since C, O, S isotope compositions might have been buffered by crustal reservoirs. 492

We suggest that some of the Martian atmospheric characteristics are consistent with a cometary origin. This possibility was proposed by Owen and Bar-Nun (1995) who noted ³⁶Ar/⁸⁴Kr/¹³²Xe similarities between the Earth and Mars despite large differences in atmospheric pressures, suggesting that a non-fractionating process supplied atmospheric noble gases to both planets. They argued that the Martian ³⁶Ar/⁸⁴Kr/¹³²Xe ratios resemble to those obtained in experimentally grown ice, and proposed impacts of icy planetesimals as the source of Martian surface volatiles. Although 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.

First, in a N vs. H isotope diagram, the atmosphere of Mars plots close to the field of comets (Fig. 502 503 2). Second, the Martian C/N, $C/^{36}$ Ar and N/ 36 Ar ratios are all close within a factor of 2 to our estimate for cometary composition (and to Earth's surface inventory, Table 4, Fig. 6), whereas the C/³⁶Ar and 504 N^{36} Ar ratios are markedly different from the chondritic values (Table 4). The δ^{15} N vs. 36 Ar/N₂ 505 isotope variations are consistent with a two-component mixing (Fig. 7). In this format, mixings 506 define straight lines (curves in the semi-log diagram of Fig. 7). Both the Martian atmosphere's δ^{15} N 507 and ³⁶Ar/N₂ values are within the estimated range of cometary ratios, and variations observed in 508 Martian meteorites define another end-member having lower $\delta^{15}N$ and higher ${}^{36}Ar/N_2$ ratios, that 509 could be chondritic and/or terrestrial contamination (preferential adsorption of nitrogen relative to 510 argon). The Kr isotope composition is solar-like, as expected for a cometary origin. After correction 511 for mass-dependent fractionation, Xe is also isotopically solar (Pepin, 1991). 512

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

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

533 **4. Conclusions and outlook**

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

For Earth, the major volatiles documented here - H₂O, C, N - were sourced mostly by material 538 akin of wet asteroids. Only a few percents at most of water, carbon and nitrogen could have 539 originated from comet-like bodies. However the terrestrial atmosphere could contain a significant, 540 possibly dominant, fraction of cometary noble gases, which might have been delivered during the 541 Terrestrial Late Heavy Bombardment around 4 Ga ago. This possibility is in line with dynamical 542 models of solar system evolution, which predict a significant fraction of icy bodies in the TLHB. 543 Resolving this question will require a better estimate of the volatile element inventory of the Earth. 544 Models that ascribe a "low" volatile content of our planet (Halliday, 2013; Dauphas and Morbidelli, 545 2014) imply that atmospheric noble gases are cometary, whereas the "high" volatile content model 546 (Marty, 2012) does not require comets and is consistent with a predominantly asteroidal (chondrtitic) 547 source (see Fig. 4b). A chondritic, rather than cometary, origin for atmospheric noble gases is 548 independently consistent with Ne-Ar isotope variations among the major terrestrial reservoirs 549

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

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

The volatile characteristics of the inner planets are consistent with trapping of protosolar nebula gas during early stages on accretion, and contributions from wet bodies from increasing heliocentric distance during the sequence of planetary building and late accretion. However no unified picture emerges for the origin(s) and processes of delivery of inner planets' atmospheric volatiles. What are now highly needed are measurements of the noble gas abundances in comets and the isotopic ratios of neon, krypton and most importantly xenon. Such measurements should be given a high priority in future cometary missions. The requested level of precision (better than percent for noble gas isotopic ratios, and per mil for stable isotopes including the three isotopes of oxygen) will require a cometary
sample return mission to permit laboratory analysis.

576 Acknowledgements

Exchanges with the members of the ROSINA Science Team helped in shaping the ideas presented 577 here. Work at UoB was funded by the State of Bern, the Swiss National Science Foundation, and by 578 the European Space Agency PRODEX Program. This work was also supported by CNES and by the 579 the European Research Council (grant no. 267255). Rosetta is an ESA mission with contributions 580 from its member states and NASA. We acknowledge herewith the work of the ESA Rosetta team. 581 BM is grateful to the University of Tokyo for supporting his visit. This work has been partly carried 582 out thanks to the support of the A*MIDEX project (n°ANR-11-IDEX-0001-02) funded by the 583 "Investissements d'Avenir" French Government program, managed by the French National Research 584 Agency (ANR). Discussions with D. Nesvorny, D. Bocquelée-Morvan, K. Mandt, E. Fueri, A. Le 585 Roy, U. Calmonte, P. Bochsler, Tobias Owen, A. Bar-Nun and members of the ROSINA Science 586 Team, helped us to shape our ideas. Constructive reviews by an anonymous reviewer, K. Mandt and 587 N. Dauphas, and efficient edition by C. Sotin are gratefully acknowledged. This is CRPG 588 contribution 2417. 589

591 References

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

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

- Chennaoui Aoudjehane, H., et al., 2012. Tissint Martian Meteorite: A Fresh Look at the Interior,
 Surface, and Atmosphere of Mars. Science 738, 785-788.
- Chyba, C.F., 1990. Impact Delivery and Erosion of Planetary Oceans in the Inner Solar System.
 Nature 343, 129–133.
- Culler, T.S., Becker, T.A., Muller, R.A., Renne, P.R., 2000. Lunar Impact History from Ar-40/Ar-39
 Dating of Glass Spherules. Science 287, 1785–188.
- 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

of Earth' Atmosphere and Oceans. Treatise Geochem. 2nd Ed., 6, 1-35.

- De Niem, D., Kührt, E., Morbidelli, A., Motschmann, U., 2012. Atmospheric Erosion and
 Replenishment Induced by Impacts upon the Earth and Mars during a Heavy Bombardment.
 Icarus 221, 495–507.
- Duprat, J., et al., 2010. Extreme Deuterium Excesses in Ultracarbonaceous Micrometeorites from
 Central Antractic Snow. Science 328, 742–745.
- Ehrenfreund, P., Charnley, S.B., 2000. Organic Molecules in the Interstellar Medium, Comets, and
 Meteorites: A Voyage from Dark Clouds to the Early Earth. Ann. Rev. Astron. Astrophys. 38,
 427–483.
- Fries, M., et al., (2016). A cometary origin for Martian Atmospheric Methane. Geochem. Perspect.
 Lett. 2, 10-23.
- Füri, E., Marty, B., 2015. Nitrogen Isotope Variations in the Solar System. Nature Geosci. 8, 515–
 522.

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

- Jacobson, S.A., Morbidelli, A., Raymond, S.N., O'Brien, D.P., Walsh, K.J., Rubie, D.C., 2014.
 Highly siderophile elements in Earth's mantle as a clock for the Moon-forming impact. Nature
 508, 84-87.
- Jakosky, B.M., Pepin, R.O., Johnson R.E., Fox. J.L., 1994. Mars Atmospheric Loss and Isotopic
 Fractionation by Solar-wind-induced Sputtering and Photochemical Escape. Icarus 111, 271 281.
- Jellinek, A.M., Jackson, M.G., 2015. Connections between the Bulk Composition, Geodynamics and
 Habitability of Earth. Nature Geosci. 8, 587–593.
- Jessberger, E.K., Cristoforidis E.A., Kissel, J., 1988. Aspects of the Major Elemental Composition
 of Halley's Dust. Nature 332, 691–695.
- Kerridge, F., 1985. Carbon, Hydrogen and Nitrogen in Carbonaceous Chondrites: Abundances and
 Isotopic Compositions in Bulk Samples. Geochim. Cosmochim. Acta 49,1707–1714.
- Kimura, K., Lewis, R.S., Anders, E., 1974. Distribution of Gold and Rhenium between Nickel-Iron
 and Silicate Melts Implications for the Abundance of Siderophile Elements on Earth and
 Moon. Geochim. Cosmochim. Acta 38, 683–701.
- Kissel J., Krueger, F.R., 1987. The Organic Component in Dust from Comet Halley as Measured by
 the PUMA Mass Spectrometer on Board Vega 1. Nature 326, 755–60.
- Le Roy, L., et al., 2015. The volatile Inventory of Comet 67P/Churyumov-Gerasimenko from
 Rosetta/Rosina. Astron. Astrophys. Sept 9, 2015, DOI: 10.1051/0004-6361/201526450.
- Levison, H.F., Dones, L., Chapman, C.R., Stern, A., 2001. Could the Lunar 'Late Heavy
 Bombardment' Have Been Triggered by the Formation of Uranus and Neptune? Icarus 151,
 286–306.

- Love, S., Brownlee, D.E., 1993. A Direct Measurment of the Terrestrial Mass Accretion Rate of
 Cosmic Dust. Science 262, 550–553.
- Mahaffy, P.R., et al., 2013. Abundance and Isotopic Composition of Gases in the Martian
 Atmosphere from the Curiosity Rovber; Science 341, 263-266.
- Marboeuf, U., Schmitt, B., 2014. How to Link the Relative Abundances of Gas Species in Coma of
 Comets to Their Initial Chemical Composition? Icarus 242, 225–248.
- Marrocchi, Y., Marty, B., 2013. Experimental Determination of the Xenon Isotopic Fractionation
 During Adsorption. Geophys. Res. Lett. 40, 4165-4170.
- Martins, Z., Botta, O., Ehrenfreund, P., 2007. Amino Acids in Antarctic CM1 Meteorites and Their
 Relationship to Other Carbonaceous Chondrites. Meteorit. Planet. Sci. 92, 81–92.
- Marty, B., et al., 2008. Helium and Neon Abundances and Compositions in Cometary Matter.
 Science 319, 75–78.
- Marty, B., 2012. The Origins and Concentrations of Water, Carbon, Nitrogen and Noble Gases on
 Earth. Earth Planet. Sci. Lett. 313-314, 56–66.
- Marty, B., Meibom, A., 2007. Noble Gas Signature of the Late Heavy Bombardment in the Earth's
 Atmosphere. eEarth 2, 43–49.
- Mc Elroy, M.B., Kong, T.Y., Yung, Y.L., 1977. Photochemistry and Evolution of Mars'
 Atmosphere: A Viking Perspective. J. Geophys. Res. 82, 4379-4388.
- Montmessin, F., Fouchet, T., Forget, F., 2005. Modeling the annual cycle of HDO in the Martian
 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 Sideronhile Elements and Core formation in the
752	Early Earth Ann Rev Earth Planet Sci 31 135–74
152	Durly Euron. Ann. Rev. Euron Funet. Ser. 51, 155 71.
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.

- Swindle, T.D., Kring, A., 2001. Implications of the noble gas budgets for the origin of water on
 Earth and Mars. Lunar Planet. Sci. Conf. # 3785.
- Sugahara, H., and Mimura, K., 2014. Glycine Oligomerization up to Triglycine by Shock
 Experiments Simulating Comet Impacts. Geochem. J. 48, 51–62.
- Takaoka, N., 1972. An Interpretation of General Anomalies of Xenon and the Isotopic Composition
 of Primitive Xenon. Mass Spectrom. 20, 287-302.
- Tera, F., Papanastassiou, D.A., Wasserburg, G.J., 1974. Isotopic Evidence for a Terminal Lunar
 Cataclysm. Earth Planet. Sci. Lett. 22, 1–21.
- Weaver, H.A., Feldman, P.D., Combi, M.R., Krasnopolsky, V. Lisse, C.M., Shemansky, D.E., 2002.
 A search for Argon and O _{VI} in Three Comets Using the Far Ultraviolet Spectroscopic Explorer.
 Astrophys. J. 576, L95-L98.
- Wetherhill, G.W., 1980. Formation of the Terrestral Planets. Ann. Rev. Astron. Astrophys. 18, 77113.
- Wong, M.H., et al., 2013. Isotopes of Nitrogen on Mars: Atmospheric Measurements by Curiosity's
 mass spectrometer. Geophys. Res. Lett. 40, 6033-6037.
- Yokochi, R., Marboeuf, U., Quirico, E., Schmitt, B., 2012. Pressure Dependent Trace Gas Trapping
 in Amorphous Water Ice at 77 K: Implications for Determining Conditions of Comet
 Formation. Icarus 218, 760–770.

	lower	upper	mean	+/-	
Water			100		1
Carbon					
CO ₂	2.5	80	41	39	2
со	1	30	16	15	2
CH₄	0.6	1.5	1.05	0.45	2
C ₂ H ₂	0.1	0.46	0.28	0.18	2
C ₂ H ₆	0.4	10.5	5.45	5.05	2
others	0.4	2.4	1.40	1.00	2
ΣC			71	65	
Nitrogen					
NH ₃	0.3	1.5	0.90	0.60	2
HCN	0.1	0.6	0.35	0.25	2
N ₂			0.088	0.083	3
ΣΝ			1.43	1.02	
$N_2/\Sigma N$			0.06	0.07	
Argon					
³⁶ Ar			1.20E-03	1.10E-03	4

Table 1: Coma composition. *1*: Species and elements are molar fractions normalized to water (=100). *2*: The range of C- and N-bearing species concentrations are for all comets analyzed so far (compiled from Bockelée-Morvan, 2011; Mumma and Charnley, 2011, Le Roy et al., 2015). *3*: The N₂ content is derived from the comet 67P measurement by Rubin et al. (2015), the good correlation between CO and N₂, and the cometary CO content given above. *4*: Ar/H₂O ratio from Balsiger et al. (2015).

789

	Coma		Bulk		792
	mole/g	+/-	mole/g	+/-	793
					,,,,
¹² C	0.012	0.011	0.037	0.028	
¹⁴ N	0.00025	0.00018	0.0018	0.0010	794
H₂O	0.017	0.0010	0.019	0.0010	
³⁶ Ar	2.07E-07	1.89E-07	2.07E-07	1.89E-07	705

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

	Atmosphere		Halliday, 2	013 - HA			Marty, 2012 - MA			Dauphas &
		Mantle	e atm.+mantle		ntle	Mantle	atm.+mantle			Morbidelli, 2015
	mol/g	mol/g	+/-	mol/g	+/-	mol/g	+/-	mol/g	+/-	DM, mol/g
¹² 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
¹⁴ 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 ₂ 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
³⁶ 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

Table 3: Earth's volatile composition. Data are in mol/g for bulk Earth (mass = 5.98×10^{27} g). 802 "Atmosphere" refers to the atmosphere sensu stricto, the oceans and crustal and sedimentary rocks 803 (data are from Ozima and Podosek, 2002, Dauphas and Morbidelli, 2014, and refs. therein). 804 Uncertainties on the C and N contents of the "atmosphere" are ~20 %. Halliday (2013; HA) 805 considered the mantle sources of MORBs and of ocean basalt islands (note that the listed abundances 806 differ from those given by Halliday, 2013, in which some of the numbers could not be reproduced). 807 Marty (2012; MA) computed volatile element abundances from K-Ar systematics which predicts 808 that, for a K content of 280 \pm 60 ppm (1 σ ; Arevalo et al 2009), half of radiogenic ⁴⁰Ar produced by 809 the decay of 40 K (T_{1/2} = 1.25 Ga) over 4.5 Ga is still trapped in the mantle. The other volatile contents 810 are computed from ⁴⁰Ar/N/C/H₂O ratio estimates for OIBs and MORBs. Dauphas and Morbidelli 811 (2014; DM) published recently estimates for volatile content of inner planets and other 812 cosmochemical reservoirs, which are intermediate between HA and MA abundances, although closer 813 to the former. HA and BM are assumed to represent two limiting cases for the Terrestrial inventory 814 of volatile elements in the silicate Earth+surface. 815

816

	Mars atm. mol/g	Carb. chondr. mol/g	Comets 818 mol/g
			819
¹² C	8.6.10 ⁻¹⁰	2.3.10 ⁻³	3.7.10 ⁻² 820
¹⁴ N	3.4.10 ⁻¹¹	6.4.10 ⁻⁵	1.8.10 ⁻³
³⁶ Ar	9.1.10 ⁻¹⁵	3.9.10 ⁻¹¹	2.1.10 ⁻⁷ ⁸²¹
			822
C/N	25	36	21
C/ ³⁶ Ar, 10 ⁴	9.5	5,900	17.9 823
N/ ³⁶ Ar, 10 ³	3.7	1,640	8.7 ₈₂₄
²⁰ Ne/ ²² Ne	7 - 10	8.5 - 12.5	? 825
δ^{15} N ‰	572 (±82)	-30 to + 150	+600 to +1,000
δD ‰	+5,500	-300 to +1,000	0 to 2,000 ⁸²⁶
<i>F_{Ne}</i> ‰/u	246	173	? 827
F _{Ar} ‰∕u	151	6	0
<i>F_{Kr}</i> ‰/u	±10	10	0 828
<i>F_{xe}</i> ‰/u	33	3	0 829

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

844 **Figure Caption**

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

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

Fig. 3: ³⁶Ar/H₂O (*a*) and ³⁶Ar/N (*b*) versus D/H mixing diagrams between cometary and chondritic (asteroidal) end-members. The mixing curves are constructed as $[X/Y]_{observed} = \alpha \times [X/Y]_1 + (1-\alpha) \times [X/Y]_2$ for two end-members having cometary/chondritic elemental/isotopic compositions. 869 Coefficients α are computed in each case using the end-member compositions (Tables 1 and 2). 870 Terrrestrial 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.

Fig. 4: D/H versus ³⁶Ar/C mixing diagram between cometary and chondritic (asteroidal) endmembers. HA, DM and MA are the bulk Earth estimates from Halliday (2013), Dauphas and Morbidelli (2014) and Marty (2012), respectively. *a*: Dotted lines indicate the percentage of Terrestrial carbon of cometary origin. *b*: Dotted lines indicate the percentage of cometary ³⁶Ar on Earth.

Fig. 5: Abundances of C, N, H₂O and ³⁶Ar in the atmosphere *sensu largo* (air+oceans+sediments), 878 normalized to Chondritic (data from Tables 2 and 3). For comparison bulk Earth inventories from 879 Table 4 are also represented. 5*a*: Effect of addition of a late veener (0.3 % of the Terrestrial mass) 880 made of 100 % comet. The ³⁶Ar inventory of the atmosphere (the main reservoir of noble gases) is 881 overabundant by several orders of magnitude, and major volatiles are also dominated by cometary 882 material. 5b: same as 3a but for a tiny contribution of cometary material in the late Veener, 883 arbitrarily chosen as 0.2 % to fit the Terrestrial abundances. 5c: Effect of contribution of a Terrestrial 884 Late Heavy Bombardment (2 x 10²³ g) made of 100 % comet. Given the uncertainties, the ³⁶Ar 885 content of the atmosphere can be matched, but the major volatiles at the Earth's surface are 886 dominated by a cometary component. 5d: A~10% cometary contribution in the TLHB fits well the 887 ³⁶Ar inventory of the atmosphere, without impacting the isotope compositions of C, N and H. 5e: 888 Effect of addition of a continuous IDP flux since 3.5 Ga ago. This flux has no impact on the 889 Terrestrial inventory of H, C, N and ³⁶Ar. 890

Fig. 6: Elemental composition of the Martian atmosphere, compared to Earth's atmosphere and 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.
- **Fig. 7:** N isotope vs. ³⁶Ar/N ratio mixing diagram between carbonaceous chondrite (CCs) and comet

end-members. The dotted curves represent mixing trajectories between Comet and CCs on one hand,

- and between MSL measured Martian atmosphric composition on another hand. between Viking and
- 898 Martian meteorite data are from Bogard et al. (2001) and refs. therein, and Chennaoui-Aoudjehane et
- al. (2012). MSL data are from Wong et al. (2013) and Mahaffy et al. (2013).

900

901







908 Fig. 1





- /12













924 Fig. 5



930 Fig. 6





