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 [a,*], Guillaume Avice [a], Yuji Sano [b], Kathrin Altwegg [c], Hans Balsiger [c], Myrtha Hässig [c], Alessandro Morbidelli [d], Olivier Mousis [e], Martin Rubin [c]

[a] Centre de Recherches Pétrographiques et Géochimiques, CRPG-CNRS, Université de Lorraine, UMR 7358, 15 rue Notre Dame des Pauvres, BP 20, 54501 Vandoeuvre lès Nancy, France
[b] Ocean and Atmosphere Research Institute, The University of Tokyo, 5-1-5, Kashiwanoha, Kashiwa-shi, Chiba 277-8564, Japan
[c] Physikalisches Institut, University of Bern, Sidlerstr. 5, CH-3012 Bern, Switzerland
[d] Laboratoire Lagrange, Université Côte d'Azur, CNRS, Observatoire de la Côte d'Azur, Boulevard de l'Observatoire, BP 4229, 06304 Nice Cedex 4, France
[e] Aix Marseille Université, CNRS, LAM (Laboratoire d'Astrophysique de Marseille) UMR 7326, 13388 Marseille, France

A B S T R A C T

Recent measurements of the volatile composition of the coma of Comet 67P/Churyumov–Gerasimenko (hereafter 67P) allow constraints to be set on the origin of volatile elements (water, carbon, nitrogen, noble gases) in inner planets' atmospheres. Analyses by the ROSINA mass spectrometry system onboard the Rosetta spacecraft indicate that 67P ice has a D/H ratio three times that of the ocean value (Altwegg et al., 2015) and contains significant amounts of N_2, CO, CO_2, and importantly, argon (Balsiger et al., 2015). Here we establish a model of cometary composition based on literature data and the ROSINA measurements. From mass balance calculations, and provided that 67P is representative of the cometary ice reservoir, we conclude that the contribution of cometary volatiles to the Earth's inventory was minor for water ($\leq 1\%$), carbon ($\leq 1\%$), and nitrogen species (a few % at most). However, cometary contributions to the terrestrial atmosphere may have been significant for the noble gases. They could have taken place towards the end of the main building stages of the Earth, after the Moon-forming impact and during either a late veneer episode 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 the noble gas isotope compositions, in particular xenon, between the mantle and the atmosphere. A mass balance based on ^{36}Ar and organics suggests that the amount of prebiotic material delivered by comets could have been quite considerable – equivalent to the present-day mass of the biosphere. On Mars, several of the isotopic signatures of surface volatiles (notably the high D/H ratios) are clearly indicative of atmospheric escape processes. Nevertheless, we suggest that cometary contributions after the major atmospheric escape events, e.g., during a Martian Late Heavy Bombardment towards the end of the Noachian era, could account for the Martian elemental C/N/^{36}Ar ratios, solar-like krypton isotope composition and high ^{15}N/^{14}N ratios. Taken together, these observations are consistent with the volatiles of Earth and Mars being trapped initially from the nebular gas and local accreting material, then progressively added to by contributions from wet bodies from increasing heliocentric distances. Overall, no unified scenario can account for all of the characteristics of the 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.

1. Introduction

According to cosmochemical constraints and simulations, the inner planets grew first "dry", and water and atmophile elements were contributed later on by volatile-rich objects originating from larger heliocentric distances (Morbidelli et al., 2000; Raymond et al., 2004; Albarède et al., 2013; Marty, 2012). A cometary origin for the Terrestrial oceans, the atmosphere and the organics is often advocated (Oro, 1961; Anders and Owen, 1977; Safronov, 1972) because (i) comets are volatile-rich as they contain abundant organics and ices (30–50 wt.% H_2O), and (ii) their high eccentricities and hyperbolic trajectories increase their probability to encounter inner solar system bodies. Other potential sources of
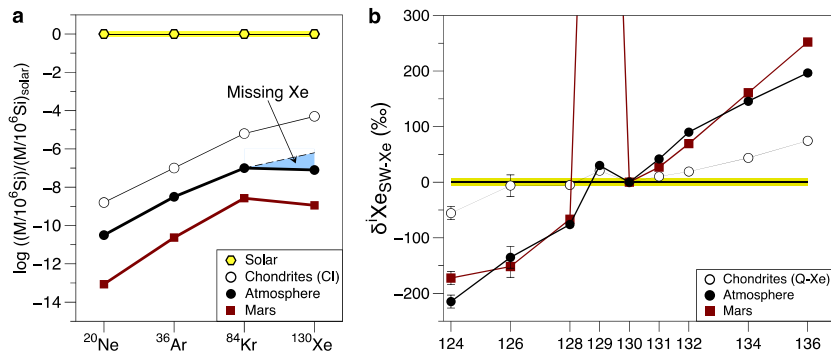
Fig. 1. (a) Comparison of the abundance patterns of noble gases in the Sun ("Solar", yellow hexagons), in volatile-rich primitive meteorites ("CI", empty circles) and in the atmospheres of Earth (black-filled circles) and Mars (red squares). Note that the latter are depleted in xenon relative to krypton and meteorites by about a factor of 20, and that the Kr/Xe is close to the solar abundance (the "missing" Xe for Earth's atmosphere is represented by the blue area, see text). Modified after Porcelli and Ballentine (2002), Mars data from Dauphas and Morbidelli (2014). (b) Comparison of the Xe isotope compositions of meteoritic Xe (empty circles, "Q–Xe"), atmospheric Xe ("Atmosphere", black-filled circles), and Martian atmosphere Xe ("Mars–Xe", red squares), expressed in deviations in parts per mil (‰) relative to the solar composition (derived from solar wind measurements, yellow bar). In this format, the solar composition gives a flat spectrum at 0‰. The meteoritic composition is slightly different from Solar, whereas Martian and Terrestrial Xe are clearly fractionated (enriched in heavy isotopes) compared to solar, prohibiting direct derivation from the protosolar nebula and, by inference, from cometary ice (see text). Data from Ott (2014). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

water are "wet" asteroids. Meteorites are generally dry, although some of them, the carbonaceous chondrite clan, can contain up to 15 wt.% equivalent H_2O as hydrated phases. Because these phases are remnant of water–rock interactions on asteroids, the original water content 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 (1.5×10^{24} g) correspond to 0.025% of the Earth's mass. Taking into account water in the deep Earth may raise the Terrestrial H_2O 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-negligible amounts of mass from asteroids and/or from icy bodies of trans-Neptunian origin, during a dynamical instability event that re-structured the orbital configuration of the giant planets (the so-called "Nice model"; Gomes et al., 2005). These models predict contributions of icy bodies in proportions comparable to those of asteroids. From the lunar impact crater record, Chyba (1990) argued that the Earth could have acquired an exogenous ocean around 4 Ga ago if comets comprised ≥ 10 wt.% of the impacting population. Marty and Meibom (2007) made the point that, if comets contain noble gases in amount predicted by laboratory ice trapping experiments (see below), then the fraction of cometary material in the late heavy bombardment on Earth could not have been more than 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. Owen and Bar-Nun (1995) noted that the noble gas elemental composition of the atmospheres of Mars and Earth (which are different from those of chondrites by having a one order of magnitude lower Xe/Kr ratio,

Fig. 1), are consistent with a cometary origin. Experiments of noble gas trapping in growing amorphous ice have shown that the absolute amounts and their relative proportions depend on the trapping kinetics, pressure and, importantly, temperature (Bar-Nun et al., 1985). Owen 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 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., 2010). Importantly, because Xe from the protosolar nebula is expected to be quantitatively trapped in cometary ice (Notesco and Bar-Nun, 2005; Yokochi et al., 2012; Mousis et al., 2010) and because physical adsorption does not induce significant Xe isotope fractionation (Marrocchi and Marty, 2013), cometary Xe should have a solar-like isotopic composition. However, the xenon isotopic compositions of the atmospheres of Earth and Mars are not solar (nor chondritic), being enriched in the heavy isotopes relative to the light ones by 3–4% par atomic mass unit (Fig. 1). Taking into account this discrepancy, Dauphas (2003) proposed a dual origin for the Terrestrial atmosphere. In his model, a primary atmosphere of solar composition was lost to space, leaving residual gases mostly made of isotopically fractionated Xe. Then comet-like bodies contributed noble gases depleted in Xe (following the same argument as Owen and Bar-Nun, 1995, that cometary ice should depleted in Xe compared to Chondritic and other noble gases, Fig. 1). This model accounts successfully for the elemental and isotopic compositions of atmospheric noble gases and for the "xenon paradox": Atmospheric xenon is depleted relative to Chondritic Xe but also relative to atmospheric Kr, and enriched in its heavy isotopes relative to any known cosmochemical composition (Fig. 1), both properties being paradoxical if xenon depletion was due atmospheric escape. However, the Xe paradox might be related to a different process and may not be a diagnostic of source composition. Indeed, from the analysis of ancient (>2.7 Ga-old) minerals, Pujol et al. (2011) argued for continuous loss and isotopic fractionation of atmospheric xenon to space through geological time as a cause of the peculiar composition of atmospheric Xe. Therefore the xenon paradox might be due to secondary long-term processing and not to a source effect.

The hydrogen and nitrogen isotopes give independent insight into the origin(s) of planetary volatiles (e.g. Alexander et al., 2012; Marty, 2012; Füri and Marty, 2015; Fig. 2). Taken together, they suggest an asteroidal, rather than cometary, origin for nitrogen
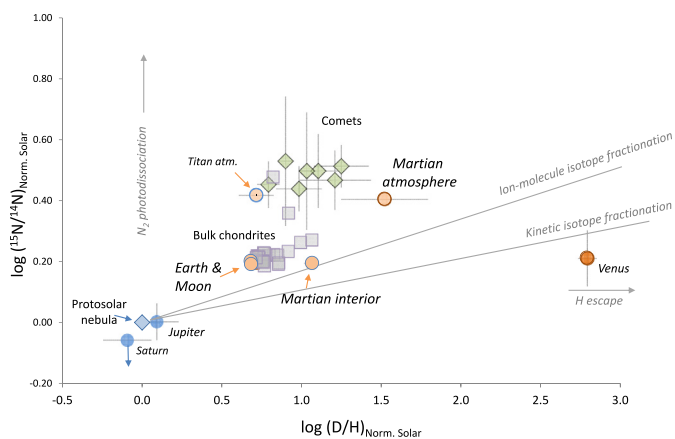
Fig. 2. Nitrogen vs. hydrogen isotope variations among solar system reservoirs (modified after Aléon, 2010, and Füri and Marty, 2015). The H and N isotopic ratios are normalized to the respective protosolar values. Fractionation trajectories are displayed for illustration. "Ion-molecule" is from Aléon (2010), representing isotope fractionation during ion molecule exchange. "Kinetic" 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 masses etc.). Light blue dots: Giant planets; beige dots: inner planets and Titan; grey squares: bulk primitive meteorites; light green diamonds: comets. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and water in the Terrestrial atmosphere and the oceans. The D/H ratios of comets are generally higher by a factor of 2–3 relative to the ocean's value and to most of the chondritic values, prohibiting a genetic relationship between cometary ice and Terrestrial water. Available data are mostly from long-period comets thought to originate from the Oort cloud. The measurement of an ocean-like D/H ratio for a Jupiter family comet (Hartogh et al., 2011), presumably originating from the Kuiper belt, suggests a D/H heterogeneity among comet families. Recently, a D/H value three times the ocean's has been measured in the coma from Comet 67P/Churyumov–Gerasimenko (thereafter 67P), also a Jupiter family member (Altwegg et al., 2015). The nitrogen isotopes give a similar story. Chondrites have variable N isotope ratios which distribution coincides with the Terrestrial composition. In contrast, 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.

2. Reservoir inventories

2.1. Comets

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.,

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 N_2 content is derived from the comet 67P measurement by Rubin et al. (2015), the good correlation between CO and N_2, and the cometary CO content given above. *4*: Ar/H_2O ratio from Balsiger et al. (2015).

	Lower	Upper	Mean	+/−	
Water			100		*1*
Carbon					
CO_2	2.5	80	41	39	*2*
CO	1	30	16	15	*2*
CH_4	0.6	1.5	1.05	0.45	*2*
C_2H_2	0.1	0.46	0.28	0.18	*2*
C_2H_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*
ΣN			1.43	1.02	
$N_2/\Sigma N$			0.06	0.07	
Argon					
^{36}Ar			1.20E−03	1.10E−03	*4*

Bockelée-Morvan, 2011; Mumma and Charnley, 2011), and (iii) laboratory analysis of cometary grains recovered by the Stardust mission (Brownlee et al., 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–aluminum rich inclusions, chondrules and refractory olivines. Stable isotope compositions of these phases indicate an inner solar system origin for this material (Brownlee et al., 2006). From mass balance, silicate + metal (Si, Mg, Fe) grains make about 25–30 wt.% (Jessberger et al., 1988). Refractory organics constitute a significant fraction of C and, to a lesser extent, of N and H, and must be taken into account in the bulk composition of cometary matter (Greenberg, 1998). This is confirmed by a refractory organics/silicate + metal ratio close to 1 for dust emitted by comet Halley (Kissel and Krueger, 1987). Therefore, organic refractory particles (the so-called CHON grains, Jessberger et al., 1988) could make another 25–30 wt.%, and non-refractory carbon-bearing species could contribute about 4–8 wt.% (Greenberg, 1998). The proportion of ice amounts for 30–50 wt.%. The composition of comae (Table 1) gives insight into the ice composition (∼80 wt.% H_2O with CO, CO_2, CH_3OH, CH_4, H_2S, and N-compounds including CN, HCN, NH_3 and N; Bockelée-Morvan, 2011; Hässig et al., 2015; Rubin et al., 2015).

Noble gases are able to set stringent constraints on the origin of planetary volatiles on one hand, and on processes and conditions of comet formation on another hand. Unfortunately the abundances of noble gases in comets are essentially unknown as these elements are extremely difficult to detect by spectroscopy. Stern et al. (2000) proposed an Ar/O ratio of $1.8 \pm 1.0 \times 10^{-4}$ for Comet Hale Bopp, lower than the solar value of 46×10^{-4} (Weaver et al., 2002, and refs. therein), but this estimate has not been confirmed. Weaver et al. (2002) suggested that the cometary Ar/O ratios are lower than 42×10^{-4}, based on three comet observations. The only reliable set of measurements are those done on 67P coma using the ROSINA mass spectrometer which directly the 67P coma composition (Balsiger et al., 2015). They indicate a

Table 2

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

	Coma (mole/g)	+/−	Bulk (mole/g)	+/−
^{12}C	0.012	0.011	0.037	0.028
^{14}N	0.00025	0.00018	0.0018	0.0010
H_2O	0.017	0.0010	0.019	0.0010
^{36}Ar	2.07E−07	1.89E−07	2.07E−07	1.89E−07

^{36}Ar/H_2O varying between 0.1×10^{-5} and 2.3×10^{-5} during the 3 days measurement period. Considering that Ar/O ~ 1.3 Ar/H_2O (Weaver et al., 2002), and taking into account a solar isotope composition for argon (^{40}Ar ~ 0, ^{38}Ar/^{36}Ar $= 0.183$), the corresponding Ar/O range of 67P is 0.01–0.35×10^{-4}, thus lower than the upper limits given above, and 2–3 orders of magnitude lower than the solar ratio of 46×10^{-4}. It is worth mentioning that even if noble gases are 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.

2.1.2. Isotopes

The stable isotope ratios relevant to this study are the D/H ratios of comets, with special reference to the 67P value ([$5.3 \pm 0.7] \times 10^{-4}$, ∼3 times the ocean water ratio; Altwegg et al., 2015), and N isotope variations depicted in Fig. 2, although no data are yet available for 67P. For noble gases, only the ^{36}Ar/^{38}Ar ratio has been measured in the coma of 67P (5.4 ± 1.6; Balsiger et al., 2015), consistent with a solar system composition, but with a precision too low to permit identification of a specific cosmochemical component. Models of ice formation from a protosolar nebula gas predict 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 isotopes, and for the local composition of the gas during ice formation. Furthermore, the analysis of Stardust refractory grains revealed a high abundance of light noble gases and has shown that the neon isotope composition is closer to a meteoritic signature than to a solar one, precluding to 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 discuss here the case of argon. The model cometary composition is given in Table 2. The uncertainties represent the range of values observed in comets, unless a single set of values is available.

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, H_2O and ^{36}Ar are, in mol/g: $2.3 \pm 1.2 \times 10^{-3}$, $6.4 \pm 2.5 \times 10^{-5}$, $3.7 \pm 1.0 \times 10^{-3}$ and $3.1 \pm 1.6 \times 10^{-11}$, respectively.

2.3. Earth

The inventory of volatile elements at the Earth's surface (the atmosphere, the oceans and the crust) is reasonably well known. The problem is to estimate the amount of volatiles in the mantle, since magmas tend to degas readily upon eruption, and the inferred source compositions are model-dependent. Recent estimates
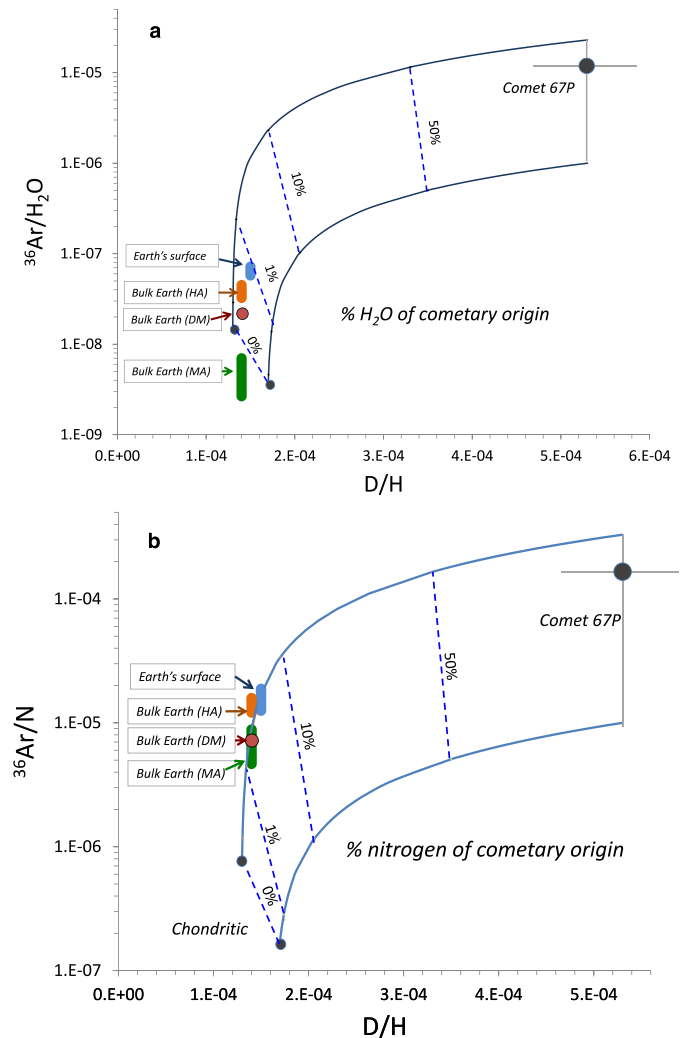

Fig. 3. ^{36}Ar/H_2O (a) and ^{36}Ar/N (b) versus D/H mixing diagrams between cometary and chondritic (asteroidal) end-members. The mixing curves are constructed as $[X/Y]_{observed} = \alpha \times [X/Y]_1 + (1 - \alpha) \times [X/Y]_2$ for two end-members having cometary/chondritic elemental/isotopic compositions. Coefficients α are computed in each case using the end-member compositions (Tables 1 and 2). Terrestrial reservoir compositions from Table 3: HA, DM and MA are the bulk Earth estimates from Halliday (2013), Dauphas and Morbidelli (2014) and Marty (2012), respectively. Dotted lines indicate the percentage of cometary water (a) and of cometary nitrogen (b), respectively, on Earth.

of the bulk Earth (mantle plus surface) volatile inventories have been given by Marty (2012), Halliday (2013) and Dauphas and Morbidelli (2014). We adopt here two limiting cases. The lower limit is based on the reconstruction of the initial volatile inventory of the mantle regions sampled by volcanism. The initial contents of water, C, N and noble gases in the mantle source of mid-ocean ridge basalts (MORB; volumetrically the main source of lavas at the Earth's surface) is derived from a combination of lava fluxes and calibration to relevant tracers like ^{3}He or refractory elements like Ce, Nb. Halliday (2013) considered also the source of Ocean Island basalts (another important source of volcanism thought to tap deep regions of the mantle), ("HA" in Figs. 3 and 4). Dauphas and Morbidelli (2014; "DM") obtained an inventory comparable to the one of Halliday (2013) from global calibration of volatiles to refractory (Ce, Nb) elements, and obtained a total bulk Earth water content of about 3 ocean masses (M_{Ocean} equivalent to 230 ppm H_2O for bulk Earth). The isotopic compositions of helium, neon, argon and xenon suggest that deep mantle regions could be richer in volatiles than the convective mantle sampled by mid-ocean ridges.

Table 3

Earth's volatile composition. Data are in mol/g for bulk Earth (mass $= 5.98 \times 10^{27}$ g). "Atmosphere" refers to the atmosphere *sensu stricto*, the oceans and crustal and sedimentary rocks (data are from Ozima and Podosek, 2002; Dauphas and Morbidelli, 2014, and refs. therein). Uncertainties on the C and N contents of the "atmosphere" are ~20%. Halliday (2013; HA) considered the mantle sources of MORBs and of ocean basalt islands (note that the listed abundances differ from those given by Halliday, 2013, in which some of the numbers could not be reproduced). Marty (2012; MA) computed volatile element abundances from K–Ar systematics which predicts that, for a K content of 280 ± 60 ppm (1σ; Arevalo et al., 2009), half of radiogenic ^{40}Ar produced by 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 are computed from ^{40}Ar/N/C/H$_2$O ratio estimates for OIBs and MORBs. Dauphas and Morbidelli (2014; DM) published recently estimates for volatile content of inner planets and other cosmochemical reservoirs, which are intermediate between HA and MA abundances, although closer to the former. HA and BM are assumed to represent two limiting cases for the Terrestrial inventory of volatile elements in the silicate Earth + surface.

	Atmosphere (mol/g)	Halliday, 2013 – HA				Marty, 2012 – MA				Dauphas and Morbidelli, 2014
		Mantle		atm. + mantle		Mantle		atm. + mantle		DM
		(mol/g)	+/−	(mol/g)	+/−	(mol/g)	+/−	(mol/g)	+/−	(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

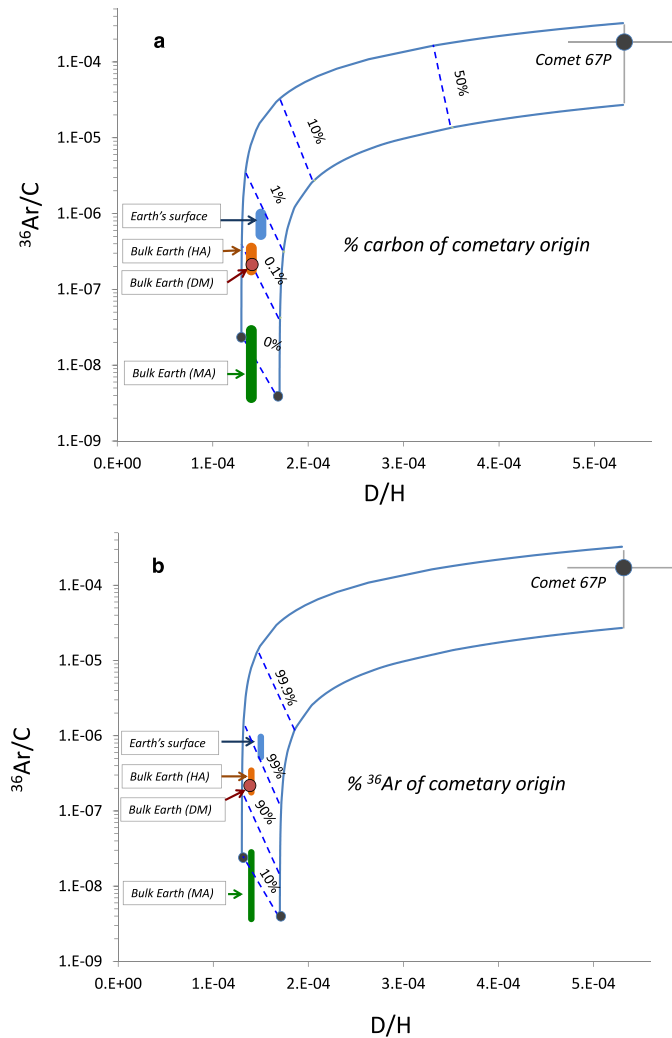**Fig. 4.** D/H versus ^{36}Ar/C mixing diagram between cometary and chondritic (aster-oidal) end-members. HA, DM and MA are the bulk Earth estimates from Halliday (2013), Dauphas and Morbidelli (2014) and Marty (2012), respectively. (a) Dotted lines indicate the percentage of Terrestrial carbon of cometary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

Table 4

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

	Mars atm. (mol/g)	Carb. chondr. (mol/g)	Comets (mol/g)
^{12}C	8.6×10^{-10}	2.3×10^{-3}	3.7×10^{-2}
^{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}
C/N	25	36	21
C/^{36}Ar, 10^4	9.5	5900	17.9
N/^{36}Ar, 10^3	3.7	1640	8.7
^{20}Ne/^{22}Ne	7–10	8.5–12.5	?
δ^{15}N‰	572 ($\pm$82)	−30 to +150	+600 to +1000
δD‰	+5500	−300 to +1000	0 to 2000
F_{Ne}‰/u	246	173	?
F_{Ar}‰/u	151	6	0
F_{Kr}‰/u	$\pm$10	10	0
F_{Xe}‰/u	33	3	0

composition of mantle domains. However, it assumes a chondritic composition for Terrestrial refractory elements. This is because the potassium content of 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 ^{40}Ar 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.

3. Discussion

3.1. How representative are cometary data?

We assume here that 67P data on one hand, and available cometary data on another hand, are representative of the compo-

K–Ar systematics indicate that about half of radiogenic ^{40}Ar produced in Earth over 4.5 Ga is still trapped in the solid Earth, the rest having been degassed into the atmosphere (Allègre et al., 1996). Calibrating volatile elements to ^{40}Ar trapped in the mantle led Marty (2012) to propose a bulk mantle ("MA") higher than the above estimates, corresponding to 4–10 ocean masses. This approach does not rely on models of the structure and the

sition of icy bodies that scattered in the inner solar system. This assumption is certainly fragile in the sense that key species measured in 67P coma are likely to vary from comet to comet. However, comets formed probably from comparable building material, water and other ice species making $\sim$30–50% of total mass. For most volatile species given in Tables 2 and 3, measurements were done spectroscopically on several comets (Mumma and Charnley, 2011; Bockelée-Morvan, 2011; Le Roy et al., 2015) so the large range of observed values is considered to be representative of the natural variability.

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 condensation/sublimation temperature. Results of their modeling indicate that, at a distance between 3 and 4 AU from the perihelion, the CO/H_2O ratio of the coma is comparable to that of the bulk comet. Argon measurements by the ROSINA mass spectrometer were done on October 19, 20, 22, and 23, 2014 when Comet 67P was at $\sim$3.1 AU from the Sun, thus possibly minimizing fractionation of minor species like Ar relative to H_2O. The 67P $^{36}Ar/H_2O$ ratio of 0.1–2.3 $\times 10^{-5}$ is also comparable to, although lower than, ratios predicted from modeling of ice trapping experiment data (2–40 $\times 10^{-5}$ in the 30–45 K range according to Dauphas, 2003; 8–75 $\times 10^{-5}$ according to Marty and Meibom, 2007, based on experimental data from Notesco and Bar-Nun, 2005). Models and experiments of noble gas trapping into cometary ice indicate that the main controlling factors on the abundance of trapped noble gases are the temperature and the partial pressures of gases (Bar-Nun et al., 1985; Yokochi et al., 2012), so that other parameters of comet formation being equal, we assume that the Ar content of cometary matter is represented by 67P data. Although the above assumptions may constitute the main weak point of the present approach, we note that uncertainty range covers one order of magnitude of the stated values (the $^{36}Ar/H_2O$ ratio) whereas the present conclusions here are based on variations of key parameters over several orders of magnitude.

3.2. Impact driven atmospheric loss

The present approach assumes that impacts are conservative, that is, contributed volatiles and target volatiles are not lost into space. This was likely not the case since giant impacts probably led to significant atmospheric loss (e.g., Genda and Abe, 2005). Recent models argue for a steady state regime between replenishment and atmospheric escape, depending on velocities, atmospheric entry 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 approach involving radiogenic ^{129}Xe, produced from the extinct radioactivity of iodine-129 ($T_{1/2} = 16$ Ma). Iodine was present when the Earth formed, as shown by the occurrence on Earth of the stable isotope ^{127}I. From meteoritic studies, it is possible to derive the solar system initial $^{129}I/^{127}I$ (1.0×10^{-4}). If the Earth formed when ^{129}I was still alive, then terrestrial reservoirs should present excesses of ^{129}Xe produced by the decay of ^{129}I. This is the case as an excess of 7% ^{129}Xe (the main reservoir of terres-

trial xenon) is present in air. This excess corresponds to about 1–2% of ^{129}Xe that could have been present if the Earth formed at the start of solar system formation. Assuming that produced ^{129}Xe was lost before the atmosphere became closed for volatile escape, one obtains a I–Xe closure age of $\sim$100 Ma after start of Solar System formation for the terrestrial system (Wetherill, 1980). Atmospheric xenon including ^{129}Xe might have been escaping from the terrestrial atmosphere for prolonged periods of time, possibly during about 2 Ga (Pujol et al., 2011), so that the ^{129}Xe excess has to be corrected for subsequent loss of atmospheric Xe. After correction, the closure age of the atmosphere becomes 30–60 Ma (Avice and Marty, 2014). A comparable budget arises when combining extinct radioactivities of ^{129}I and ^{244}Pu ($T_{1/2} = 82$ Ma), implying that Xe loss was early, 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 exceeded 60–80% of atmospheric Xe, and probably less after the Moon-forming impact which occurred within 40–90 Ma after start of Solar System formation. We tentatively conclude that the atmosphere was grossly conservative, within a factor of two, after the Moon-forming impact (the period of time relevant to cometary contributions, see next sub-sections).

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 ^{36}Ar and H_2O in comets (they took the Hale Bopp's $^{36}Ar/O$ 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 Earth and Mars. Dauphas (2003) noted that the low Xe/H_2O ratio of the Earth compared to other cosmochemical end-members could set stringent constraints on the maximum amount of cometary water on Earth. Since then, it has been proposed that the low terrestrial Xe/H_2O ratio could be secondary (Pujol et al., 2011), making the argument less constraining. Figs. 3 and 4 represent mixing curves between chondritic and cometary end-members using the $^{36}Ar/X$ (where X represents water, nitrogen or carbon) ratio versus the D/H ratio. In fact the ^{36}Ar concentration is more sensitive than the D/H ratio alone, because contribution of 67P-like material can strongly impact the atmospheric inventory of argon. For water, a cometary contribution of the order of 1% or less is allowed depending on the bulk silicate Earth + surface composition (Fig. 3a), confirming that Terrestrial 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 (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 NH_2 (the latter presumably from NH_3) are all enriched by a factor of 2 in ^{15}N relative to ^{14}N (e.g., Füri and Marty, 2015, for a review). However, other N species like N_2 (Rubin et al., 2015) and refractory organics are present in comets with unknown N isotope composition, preventing to establish an isotope budget for the cometary reservoir.

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.

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 abundance pattern of the atmosphere, and by Marty and Meibom (2007) from mass balance considerations. For the bulk silicate Earth inventory, the conclusion depends on the adopted composition. For the HA and DM inventories, a major cometary origin for argon is clearly possible (Fig. 4b). The MA inventory does not require contribution of cometary noble gases to the bulk Earth (Fig. 4b). In this model, noble gases are mostly in the atmosphere, and major volatiles (H_2O, C) are in the mantle, the sum of which being consistent with the addition of ∼2 wt.% of carbonaceous chondrite type material.

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

4. The Terrestrial late heavy bombardment (TLHB) is an extrapolation of the late heavy bombardment thought to have occurred on the Moon from the size-age distribution of lunar craters (Tera et al., 1974). Estimates of the mass contribution to Earth during the TLHB, based on the Lunar cratering record, range from 2.2×10^{23} g (Hartmann et al., 2002) down to 4×10^{22} g (assuming

that the TLHB started at the time of formation of Nectaris basin; Morbidelli et al., 2012). From a modeling approach, Levison et al. (2001) proposed a mass contribution of 8×10^{22} g. Gomes et al. (2005) estimated a TLHB of 4×10^{23} g, about half of which being cometary. The newest version of the Nice model, however, reduces the mass flux to the Earth to about 4×10^{22} g of asteroidal material (Bottke et al., 2012) and $2–4 \times 10^{22}$ g of cometary material (depending on the dynamical state of the trans-Neptunian disk before the dynamical instability). For the calculations presented here, a conservative value of 2.0×10^{23} g is adopted. Marty and Meibom (2007) concluded that less than 1% comets were present in the TLHB, the rest being asteroidal material, and proposed that atmospheric noble gases could constitute the only remaining evidence for the TLHB. Their mass balance was based on noble gas cometary concentration from ice trapping experiments, which are higher than the one constrained by Ar in 67P. With the ROSINA ^{36}Ar measurement, a 100% cometary TLHB would supply too much ^{36}Ar to the atmosphere (Fig. 5c). It would also supply most major volatiles at the 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 ∼2.0×10^{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 ∼2×10^{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).

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

From isotope geochemistry considerations, several distinct cosmochemical sources contributed noble 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.

(ii) The isotopic compositions of H, N and mantle Kr isotopes are consistent with a chondritic 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 secondary and may not be a source signature (Pujol et al., 2011; Avice and Marty, 2014). Even when corrected for mass-dependent fractionation, the atmospheric Xe isotope composition cannot be derived from either Solar or Chondritic, because it is depleted in the heavy isotopes ^{134}Xe and ^{136}Xe relative to the latter. Secondary (nuclear) processes such as fission of heavy radionuclides can only enrich, and not deplete, these isotopes. This observation led Takaoka (1972) and Pepin (1991) to postulate the existence of a distinct primordial Xe having sourced the Terrestrial atmosphere (the Xe–U component of Pepin, 1991). This mass-independent isotope fractionation of Xe isotopes might have resulted from an unknown nuclear effect, or from a different
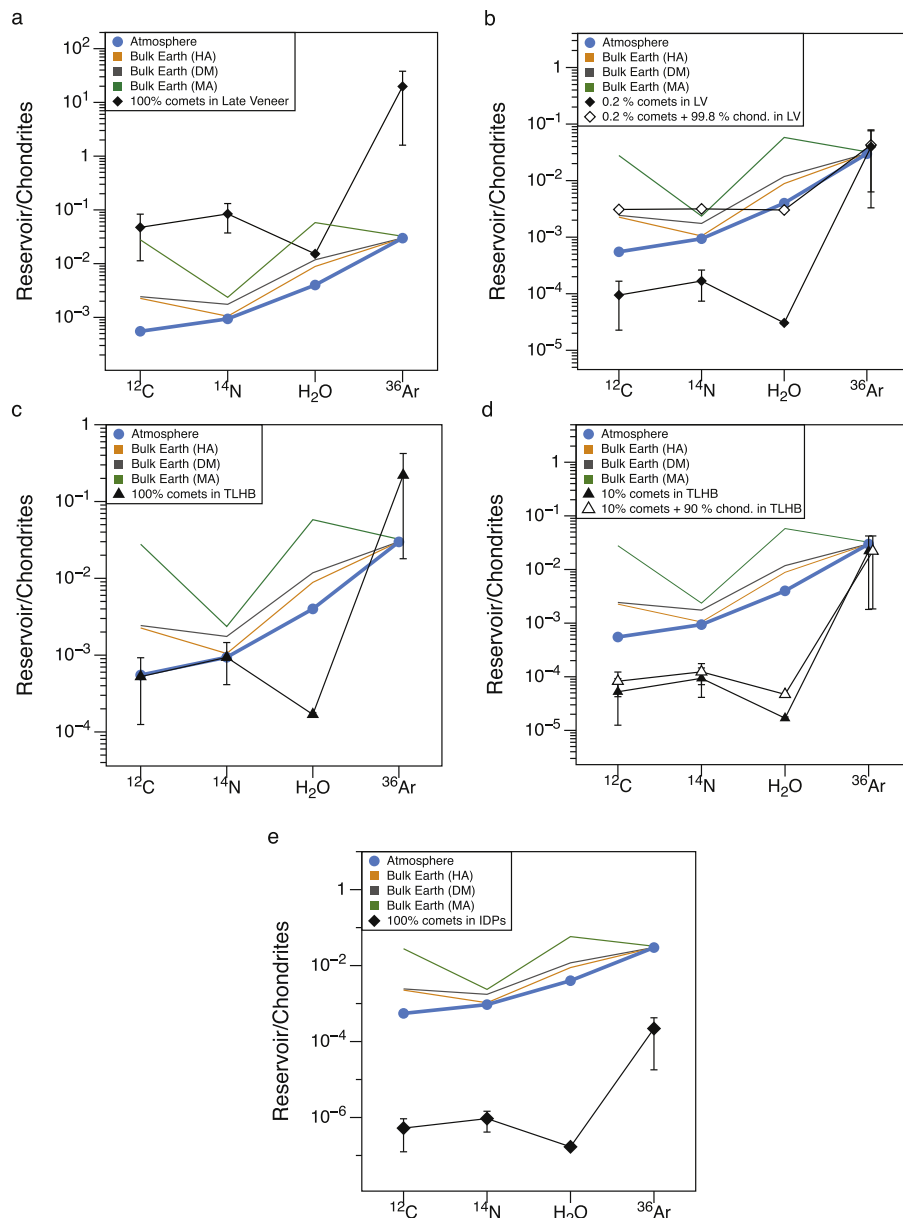
Fig. 5. Abundances of C, N, H_2O and ^{36}Ar in the atmosphere *sensu largo* (air + oceans + sediments), normalized to Chondritic (data from Tables 2 and 3). For comparison bulk Earth inventories from Table 4 are also represented. (a) Effect of addition of a late veneer (0.3% of the Terrestrial mass) made of 100% comet. The ^{36}Ar inventory of the atmosphere (the main reservoir of noble gases) is overabundant by several orders of magnitude, and major volatiles are also dominated by cometary material. (b) Same as 3a but for a tiny contribution of cometary material in the late Veneer, arbitrarily chosen as 0.2% to fit the Terrestrial abundances. (c) Effect of contribution of a Terrestrial Late Heavy Bombardment (2×10^{23} g) made of 100% comet. Given the uncertainties, the ^{36}Ar content of the atmosphere can be matched, but the major volatiles at the Earth's surface are dominated by a cometary component. (d) A ~10% cometary contribution in the TLHB fits well the ^{36}Ar inventory of the atmosphere, without impacting the isotope compositions of C, N and H. (e) Effect of addition of a continuous IDP flux since 3.5 Ga ago. This flux has no impact on the Terrestrial inventory of H, C, N and ^{36}Ar.

mix of nucleosynthetic components that were not fully homogenized during solar system formation.

Given the possible cometary origin of atmospheric noble gases, we speculate that this exotic Xe component could have been carried out from the outer solar system to its inner region by icy bodies. The dichotomy between mantle chondritic Xe and surface Xe would then be a record of Terrestrial 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 ^{36}Ar (5.55×10^{15} moles, Ozima and Podosek, 2002), a cometary contribution between 3×10^{21} and 6.5×10^{23} g would have been necessary (computed with a ^{36}Ar

cometary concentration of $2.1 \pm 1.9 \times 10^{-7}$ mol/g, and a cometary density of 0.5 from the 67P measurements). This is in great agreement with the most recent 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 a higher ^{36}Ar content of comets. The impact of a single cometary body with a radius of 100–300 km, or of a limited number of smaller bodies, could have sufficient to supply all atmospheric argon. Therefore, it may be possible that the supply of atmospheric volatiles to the Terrestrial planets was a stochastic process involving a small population of objects, which might have resulted in a heterogeneous distribution of outer solar system

isotopic signatures. In this respect, the high abundance of ^{36}Ar in the atmosphere of Venus could effectively be the result of random contribution of cometary material ton inner planets.

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

3.8. The case of the Martian atmosphere

The composition of the atmosphere of Mars (Table 4) is reasonably known from the in-situ analyses by the Viking and the Mars Science Laboratory (MSL) landers, and from the analysis of some of the Martian meteorites which contain atmospheric volatiles trapped in impact glasses (see Bogard et al., 2001, for a comprehensive review, and Wong et al., 2013, and refs. therein, for recent Curiosity MSL data). Compared to Earth and bulk meteorites, the Martian atmosphere is rich in ^{15}N (δ^{15}N $= 572 \pm 82\permil$ relative to the Terrestrial atmosphere, Wong et al., 2013) and in deuterium (δD $= 5500\permil$ relative to the oceans; Bogard et al., 2001; Montmessin et al., 2005, and refs. therein; Fig. 2). Likewise, neon, argon (^{36}Ar, ^{38}Ar) and xenon isotopic signatures are enriched in their heavy isotopes by 246, 151, and 33‰, respectively, relative to the solar compositions (Table 4). In contrast, volatiles in the Mars interior, also analyzed in Martian meteorites, have isotopic ratios comparable to inner solar system signatures (Fig. 2).

The atmospheric signatures have been interpreted as resulting from isotope fractionation during atmospheric escape processes. Possibilities include solar wind-induced photochemical reactions producing electrons able to dissociate N_2 for nitrogen (McElroy et al., 1977), and sputtering for the noble gases (Jakosky et al., 1994). Chassefière and Leblanc (2004) reviewed potential escape mechanisms that might have affected the atmosphere of Mars and

concluded that (i) not a single 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. Atmospheric loss is attested by morphological evidence on Mars indicating past water flows (Carr and Head, 2003), and major escape processes might have taken towards the end of the Noachian period 4.0–3.7 Ga ago. Thus escape-related fractionation of Martian volatiles is likely to have played a key role in fractionating elemental abundances and isotopic compositions. Nevertheless, we suggest here that possible source effects, namely cometary contributions, should be also considered, especially after the major escape events that resulted in a tenuous atmosphere on Mars.

Several key observations are not entirely consistent with atmospheric escape as a cause of isotopic enrichments. (i) The noble gas elemental abundance of the Martian atmosphere and the C/N ratio (Pepin, 1991) are comparable to those of Venus and Earth (for which similar escape fractionations are unlikely). (ii) The krypton isotopic composition of the Martian atmosphere is close to the solar composition (Bogard et al., 2001, and refs. therein), contrary to those of Ne, Ar and Xe (Table 4). Because the mass of Kr is intermediate between those of Ne, Ar and Xe, this difference points to other processes than escape-related fractionation. We note that the Martian Ne isotopic composition is within the range of chondritic values, e.g., the so-called Ne–A (planetary) component of carbonaceous chondrites. Neon is not expected to be trapped in comets, so that Martian atmospheric Ne could have been sourced by an another cosmochemical reservoir. The high ^{38}Ar/^{36}Ar ratio (0.238 ± 0.005; Atreya et al., 2013) is indeed a good diagnostic of escape-related fractionation, but cosmic-ray production of noble gas isotopes (which also increases this ratio) could have been significant for 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 Terrestrial atmospheric Xe (Pujol et al., 2011). (iv) The isotopes of C, O, S in the Martian surface and crust are little fractionated. CO_2 is enriched in ^{13}C relative to Terrestrial (δ^{13}C $= 46 \pm 4\permil$; Mahaffy et al., 2013) but to a much lesser extent than ^{15}N in nitrogen (δ^{15}N $= 572 \pm 82\permil$, Wong et al., 2013). However this argument is not carved in stone since C, O, S isotope compositions might have been buffered by crustal reservoirs.

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 ^{36}Ar/^{84}Kr/^{132}Xe 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 ^{36}Ar/^{84}Kr/^{132}Xe 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 Xe fractionation could result from Xe-specific non-thermal processing like on Earth, Pujol et al., 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. 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/^{36}Ar and N/^{36}Ar ratios are markedly different from the chondritic values (Table 4). The δ^{15}N vs. ^{36}Ar/N_2 isotope variations are consistent with a two-component mixing (Fig. 7). In this format, mixings define straight lines (curves in the semi-log diagram of Fig. 7). Both the Martian atmosphere's δ^{15}N and ^{36}Ar/N_2 values are within the estimated range of cometary ratios, and variations observed in Martian meteorites define an-
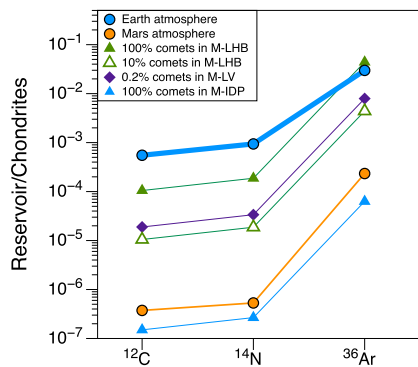
Fig. 6. Elemental composition of the Martian atmosphere, compared to Earth's atmosphere and comets. Data sources: Pepin (1991), Bogard et al. (2001), Dauphas and Morbidelli (2014). Water is not represented here since its Martian inventory is unknown. The effects of a Martian late veneer (M–LV), a Martian Late Heavy Bombardment (M–LHB) and continuous IDP flux are also represented.
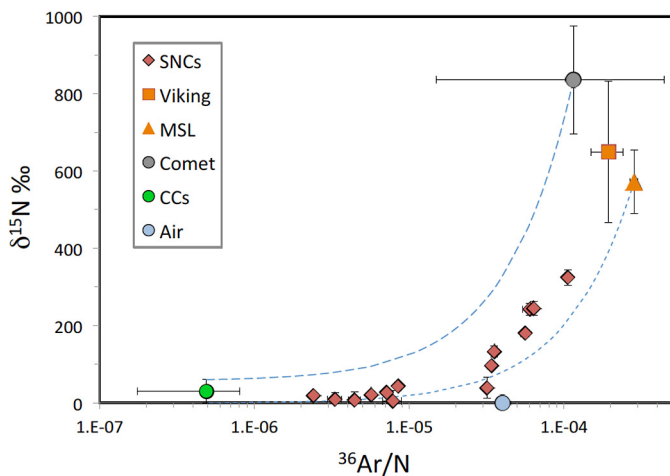

Fig. 7. N isotope vs. $^{36}Ar/N$ ratio mixing diagram between carbonaceous chondrite (CCs) and comet end-members. The dotted curves represent mixing trajectories between Comet and CCs on one hand, and between MSL measured Martian atmospheric composition on another hand. Between Viking and Martian meteorite 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).

other end-member having lower $\delta^{15}N$ and higher $^{36}Ar/N_2$ ratios, that could be chondritic and/or terrestrial contamination (preferential adsorption of nitrogen relative to argon). The Kr isotope composition is solar-like, as expected for a cometary origin. After correction for mass-dependent fractionation, Xe is also isotopically solar (Pepin, 1991).

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

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

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 – H_2O, C, N – were sourced mostly by material akin of wet asteroids. Only a few percents at most of water, carbon and nitrogen could have originated from comet-like bodies. However the terrestrial atmosphere could contain a significant, possibly dominant, fraction of cometary noble gases, which might have been delivered during the Terrestrial Late Heavy Bombardment around 4 Ga ago. This possibility is in line with dynamical models of solar system evolution, which predict a significant fraction of icy bodies in the TLHB. Resolving this question will require a better estimate of the volatile element inventory of the Earth. Models that ascribe a "low" volatile content of our planet (Halliday, 2013; Dauphas and Morbidelli, 2014) imply that atmospheric noble gases are cometary, whereas the "high" volatile content model (Marty, 2012) does not require comets and is consistent with a predominantly asteroidal (chondritic) source (see Fig. 4b). A chondritic, rather than cometary, origin for atmospheric noble gases is independently consistent with Ne–Ar isotope variations among the major terrestrial reservoirs including the atmosphere (Marty, 2012). This problem may appear too specialized for a non-specialist audience, but there are outstanding issues beyond it, such as the origin of prebiotic material on Earth (which could be traced with noble gases), the early processes of volatile delivery and escape, the timing of volatile delivery (which can be addressed with noble gas radiogenic isotopes), and the composition and mode of transfer of material from the outskirts of the Solar System. For example, the isotopic composition of atmospheric xenon cannot be simply related to either the solar nebula or asteroidal material. It requires a specific composition (U–Xe; Pepin, 1991) that could trace nucleosynthetic heterogeneities in outer solar system bodies. Resolving these important issues will require a better estimate of the volatile content of the mantle on the one hand, as well as precise cometary noble gas data including isotopes on the other hand.

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.

Acknowledgements

References

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, 721–723.

Allègre, C.J., Hofmann, A.W., O'Nions, R.K., 1996. The argon constraints on mantle structure. Geophys. Res. Lett. 23, 3555–3557.

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, 453–465.

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. Philos. Trans. R. Soc., Math. Phys. Eng. Sci. 372, 20130260.

Balsiger, H., et al., 2015. Detection of argon in the coma of comet 67P/Churyumov–Gerasimenko. In: Science Advances, vol. 1.

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. Orig. Life Evol. Biosph. 31, 15–51.

Bockelée-Morvan, D., 2011. An overview of comet composition. In: Proceed. Intern. Astron. Union, vol. 7, pp. 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., et al., 2012. An Achaean heavy bombardment from a destabilized extension of the asteroid belt. Nature 485, 78–81.

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.

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. http://dx.doi.org/10.1029/2002JE001963.

Chassefière, E., Leblanc, F., 2004. Mars atmospheric escape and evolution: interaction with the 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 ^{40}Ar–^{39}Ar dating of glass spherules. Science 287, 1785–1788.

Dauphas, N., 2003. The dual origin of the terrestrial atmosphere. Icarus 165, 326–339.

Dauphas, N., Morbidelli, A., 2014. Geochemical and planetary dynamical views on the origin of Earth' atmosphere and oceans. In: Treatise Geochem., vol. 6, 2nd ed., pp. 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 Antarctic 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. Annu. 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. Nat. 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: Canup, R.M., Righter, K. (Eds.), Origin of the Earth and Moon. Univ. Arizona Press, pp. 451–493.

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/Churyumov–Gerasimenko. Science 347 (6220). aaa0276-1.

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. Nat. 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, 755–760.

Le Roy, L., et al., 2015. The volatile inventory of comet 67P/Churyumov–Gerasimenko from Rosetta/Rosina. Astron. Astrophys. 9. http://dx.doi.org/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 measurement 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., 2012. The origins and concentrations of water, carbon, nitrogen and noble gases on Earth. Earth Planet. Sci. Lett. 313–314, 56–66.

Marty, B., et al., 2008. Helium and neon abundances and compositions in cometary matter. Science 319, 75–78.

Marty, B., Meibom, A., 2007. Noble gas signature of the late heavy bombardment in the Earth's atmosphere. eEarth 2, 43–49.

McElroy, 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.

Morbidelli, A., et al., 2000. Source regions and timescales for the delivery of water to the Earth. Meteorit. Planet. Sci. 35, 1309–1320.

Morbidelli, A., Marchi, S., Bottke, W.F., Kring, D.A., 2012. A sawtooth-like timeline for the first billion years of lunar bombardment. Earth Planet. Sci. Lett. 355, 144–151.

Mousis, O., et al., 2010. Impact regimes and post-formation sequestration processes: implications for the origin of heavy noble gases in terrestrial planets. Astrophys. J. 714, 1418–1423.

Mumma, M.J., Charnley, S.B., 2011. The chemical composition of comets – emerging taxonomies and Natal heritage. Annu. Rev. Astron. Astrophys. 49, 471–524.

Notesco, G., Bar-Nun, A., 2005. A ∼25 K temperature Fo formation for the submicron ice grains which formed comets. Icarus 175, 546–550.

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

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

Oro, J., 1961. Comets and the formation of biochemical compounds on the primitive Earth. Nature 190, 389–390.

Ott, U., 2014. Planetary and pre-solar noble gases in meteorites. Chem. Erde 74, 519–544.

Owen, T., Bar-Nun, A., 1995. Comets, impacts and atmospheres. Icarus 116, 215–226.

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

Pepin, R.O., 1991. On the origin and early evolution of terrestrial planet atmospheres and meteoritic volatiles. Icarus 92, 2–79.

Porcelli, D., Ballentine, C.J., 2002. Models for the distribution of terrestrial noble gases and evolution of the atmosphere. Rev. Mineral. Geochem. 47, 411–480.

Pujol, M., Marty, B., Burgess, R., 2011. Chondritic-like xenon trapped in Archean rocks: a possible signature of the ancient atmosphere. Earth Planet. Sci. Lett. 308, 298–306.

Raymond, S.N., Quinn, T., Lunine, J.I., 2004. Making other earths: dynamical simulations of terrestrial planet formation and water delivery. Icarus 168, 1–17.

Raymond, S.N., Quinn, T., Lunine, J.I., 2007. High-resolution simulations of the final assembly of Earth-like planets. 2. Water delivery and planetary habitability. Astrobiology 7, 66–84.

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

Righter, K., 2003. Metal–silicate partitioning of siderophile elements and core formation in the early Earth. Annu. Rev. Earth Planet. Sci. 31, 135–174.

Rubin, M., et al., 2015. Molecular nitrogen in comet 67P/Churyumov–Gerasimenko indicates a low formation temperature. Science 348, 232–235.

Safronov, V.S., 1972. The motion, evolution and origin of comets. In: Chebotarev, G.A. (Ed.), The Motion, Evolution and Origin of Comets. Springer-Verlag, pp. 329–334.

Schlichting, H.E., Sari, R., Yalinewich, A., 2014. Atmospheric mass loss during planet formation: the importance of planetesimal impacts. Icarus 247, 81–94.

Schultz, L., Franke, L., 2004. Helium, neon, and argon in meteorites: a data collection. Meteorit. Planet. Sci. 39, 1889–1890.

Stern, S.A., et al., 2000. The discovery of argon in comet C/1995 O1 (Hale Bopp). Astrophys. J. 544, L169–L172.

Sugahara, H., Mimura, K., 2014. Glycine oligomerization up to triglycine by shock experiments simulating comet impacts. Geochem. J. 48, 51–62.

Swindle, T.D., Kring, A., 2001. Implications of the noble gas budgets for the origin of water on Earth and Mars. In: Lunar Planet. Sci. Conf. Abstr. #3785.

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.

Wetherill, G.W., 1980. Formation of the terrestrial planets. Annu. Rev. Astron. Astrophys. 18, 77–113.

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.