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Origin of life-forming volatile elements in the inner Solar System

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Volatile elements such as hydrogen, carbon, nitrogen and oxygen are essential ingredients to build habitable worlds like Earth, but their origin and evolution on terrestrial planets remain highly debated. Here we discuss the processes that distributed these elements throughout the early Solar System and how they then became incorporated into planetary building blocks. Volatiles on Earth and the other terrestrial planets appear to have been heterogeneously sourced from different Solar System reservoirs. The sources of planetary volatiles and the timing at which they were accreted to growing planets probably play a crucial role in controlling planet habitability.

Our Solar System emerged 4.567 billion years ago (Ga) as the result of the gravitational collapse of a molecular cloud core¹, resulting in a more than 30-AU-wide disk of gas (99 wt%) and dust (1 wt%), hereafter referred to as the protosolar nebula (PSN)². The first solids that went on to form the planetary building blocks and eventually the first planets materialized as a result of condensation from the PSN, together with a small contribution of presolar material inherited from the interstellar medium^{3,4}. Primitive asteroids (sampled on Earth in the form of ‘chondritic’ meteorites) and comets found today in the Solar System are made up of an assortment of these early building blocks and have remained limitedly processed since their original formation at the dawn of the Solar System (Fig. 1). Yet, volatile elements (defined by their exceptionally low melting point), including hydrogen (H), carbon (C), nitrogen (N) and oxygen (O), trapped in chondrites, comets and the atmospheres of the terrestrial planets have elemental and isotopic compositions markedly different from those of the PSN. This therefore excludes the possibility that the building blocks that make up the terrestrial planets accreted volatiles directly from the gaseous solar nebula, without prior modification (Fig. 2 and Box 1). In addition to having a non-solar volatile composition, planetary building blocks show large variations in elemental and isotopic compositions, illustrating the complex nature of volatile distribution and processing in the PSN (Box 1). These observations raise fundamental questions on (1) how heterogeneous solid materials formed from the isotopically homogeneous, solar-like gas phase of the PSN (‘Volatile incorporation in early solids’), (2) which processes heterogeneously distributed volatiles throughout the early Solar System (‘Volatile diversity in early Solar System’), and finally (3) how volatiles from the PSN and those carried in early-formed solid materials were accreted to, and survived on, planetary bodies including Earth, during the main (‘Volatile evolution during accretion’) and late (‘Terminal stages of volatile accretion’) accretionary stages. Although many excellent reviews of early Solar System processes and the mechanics of planetary formation exist^{5–10}, we provide here a more volatile-centric view on how these different processes resulted in the assortment of terrestrial planets that we know today, and what makes Earth unique among the Solar System. We outline how recent advances in geochemical analysis of terrestrial and extraterrestrial samples (for example, meteorites or space missions), together with laboratory experiments, astrophysical observations and numerical modelling,

have transformed our understanding of the distribution of volatile elements in the early Solar System and the processes that resulted in their eventual incorporation into planetary bodies.

Volatile incorporation in early solids

One of our best avenues to investigate the early Solar System and how solid materials obtained volatiles from the surrounding PSN is through the analysis of chondritic meteorites and their constituents, most of which condensed out of the cooling gas of the PSN, although a small fraction was inherited directly from the interstellar medium (Fig. 1). From the analysis of primitive extraterrestrial materials, trapped in chondrites and comets, it is thought that volatiles were predominantly incorporated into growing planetary bodies in the form of ices, organics and hydrated silicates¹¹. Determining how these volatile-bearing phases formed and evolved within the PSN is therefore vital to our understanding of how volatiles were accreted to planets including Earth.

A key feature of our Solar System is that planetary bodies are consistently and severely depleted in volatile elements relative to the PSN (Fig. 2). Furthermore, the isotopic signature of these volatiles are markedly different from the composition of the starting gas, with all the terrestrial planets being enriched in the heavy and rare isotopes relative to the PSN (Box 1). This suggests that the material that made up the terrestrial planets originated from cosmochemical reservoirs that were either distinct from the PSN, or subjected to processes that altered their original, PSN-like composition. Large-scale isotopic heterogeneities measured across the Solar System could therefore reflect the series of processes that were instrumental in the formation and evolution of H-, C-, N- and O-bearing solid phases, from the molecular cloud to planets.

The potential for heterogeneous inheritance of nucleosynthetically anomalous, presolar material to produce the isotopic variability in volatiles throughout our Solar System (Box 1) can for the most part be disregarded, as the same variability is not witnessed in moderately volatile (for example, potassium¹²) and refractory (for example, molybdenum¹³) elements. Ion–molecule exchange reactions at low temperature in dense molecular clouds, which favour the heavy isotopes in the reactants^{14,15}, could explain some of the deuterium (D) enrichments found in molecular cloud ices^{16,17} and organics¹⁸, respectively. In this context, at least part of the H, and potentially C, N and O, isotopic variations across the Solar System could

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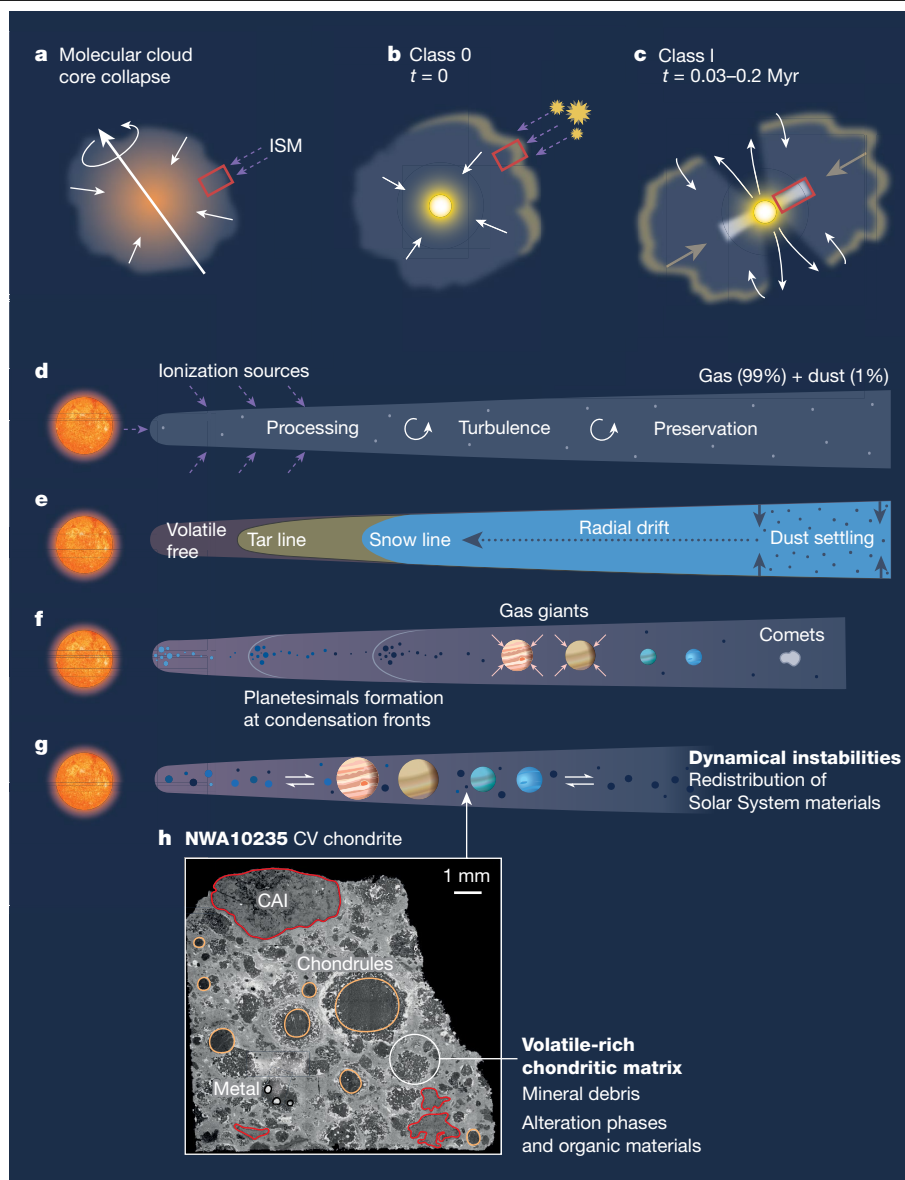


Fig. 1 | The main steps of PSN formation from the collapse of the molecular cloud core until planet formation, and the associated processes controlling H, C, N and O distribution and isotopic fractionation. a–c. The different steps of molecular cloud core collapse (a) and formation of the PSN from stellar class 0 (b) to class I (c). The red rectangles indicate potential locations of ionization and/or self-shielding effects in the molecular cloud (a,b) and PSN (c). **d–g.** The chemical and dynamical evolution of the PSN. **d.** Gas and dust are processed and distributed throughout the PSN by turbulent mixing. **e.** The spatial distribution of H, C and N in their solid form is then mainly controlled by the location of the tar and snow lines. **f.** The early accretion of planetesimals (kilometre-sized to hundred-kilometre-sized solid bodies) then occurs at localized pressure bumps. **f,g.** Planetary formation continues by the rapid

growth (f) and potential gas-driven migration (g) of the gas giants, which destabilizes the orbits of nearby bodies leading to the scattering of outer Solar System material towards the terrestrial planet accretion region (see review by ref.¹⁰³). **h.** A backscattered electron image of a cross-section of the CV (Vigarano type) chondrite NWA (North West Africa) 10235 containing the three main components of chondrites: (1) calcium–aluminium-rich inclusions (CAIs), the first mineral assemblages that condensed from the PSN^{141,142}, (2) chondrules, (sub)millimetre-sized igneous spherules that represent the major constituent of chondrites (up to 85 vol%), and (3) the matrix, a heterogeneous assemblage of mineral debris, alteration phases and organic materials, containing the vast majority of volatiles in chondrites. Panels a–c adapted with permission from ref.¹⁴⁰, Wiley.

represent the preservation of pristine fingerprints of molecular cloud chemistry, with the outer Solar System having better preserved unprocessed (D and ¹⁵N rich) material than the hotter, inner regions¹⁹ (Fig. 1).

Being by far the most abundant element in rock-forming minerals of the Solar System (about 47% (ref.²⁰)), O is a tracer of the origin and evolution of not only volatile-bearing phases in the PSN but also nearly all solid material. Oxygen has three isotopes, and its two rarer isotopes, ¹⁷O and ¹⁸O, can be normalized to the abundant ¹⁶O isotope. In many of the Solar System objects and reservoirs, $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ variations have been shown to follow mass-independent isotope fractionation (MIF),

implying that mass-dependent fractionation during ion–molecule reactions advocated above for H and N cannot explain O isotope variations. Oxygen MIF in the Solar System could potentially arise from photon–gas interactions, as substantiated by laboratory experiments²¹. One possibility is self-shielding, which occurs when stellar photons penetrate a cloud of gas and become selectively absorbed by photoreactions²². As ¹⁶O is more abundant compared with ¹⁷O and ¹⁸O, ultraviolet photons of energy allowing for the specific dissociation of C¹⁶O become rapidly depleted by absorption compared with those dissociating C¹⁷O and C¹⁸O. Consequently, in gas environments with sufficiently high

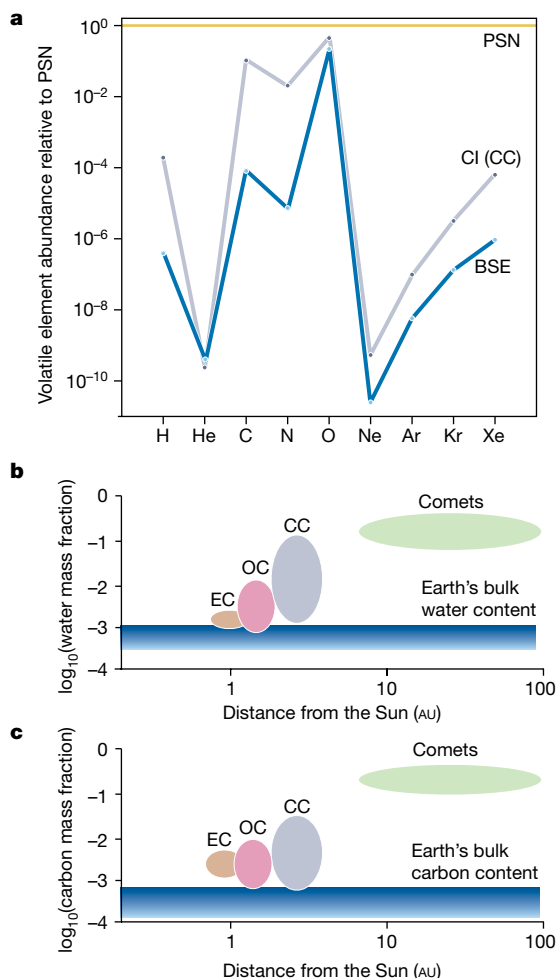


Fig. 2 | Abundance and distribution of volatile elements in planetary bodies of the Solar System. **a.** Absolute volatile element abundances in CI chondrites—the most primitive volatile-rich chondrite type—and BSE (the bulk chemical composition of Earth from which the core has been subtracted) normalized to the elemental composition of the PSN. Before normalization, all concentrations are expressed in atoms per million atoms of silicon^{8,20}. **b,c.** Range of water (**b**) and carbon (**c**) mass fractions of Earth, chondritic meteorite parent bodies (with EC, OC and CC corresponding to enstatite, ordinary and carbonaceous-type chondrites, respectively) and comets. These depict a radial gradient (expressed in astronomical units, AU, corresponding to the Earth–Sun distance) in the abundance of the two main carrier phases of volatile elements in the Solar System: ice and organic materials. Panels **b** and **c** adapted with permission from ref.¹⁴³, Annual Reviews Inc., with data from <https://doi.org/10.24396/ORDAR-66>.

carbon monoxide (CO) abundances, photodissociation of molecules hosting ¹⁷O and ¹⁸O takes place deeper in the cloud than for ¹⁶O. Hence, self-shielding is a line-dominated process that could have taken place in both the parent molecular cloud illuminated by nearby stars²³ and/or at the disk surface of the PSN with photons from the nascent Sun²⁴ (red rectangles in Fig. 1a–c). Photodissociation of gaseous CO could represent a significant source of atomic C and O that could react with H₂ to form hydrocarbons (C_xH_y molecules) and water (H₂O) molecules, respectively, therefore providing an effective pathway for the formation of ¹⁶O-depleted solid phases including ice and organics, which represent the main inventory of volatiles in early forming planetesimals.

A photochemical origin for organic material in meteorites is consistent with the observation of D and/or ¹⁵N enrichments²⁵, oxygen MIF²⁶, as well as noble gas systematics in chondrites^{27,28}. Notably, organo-synthesis triggered by organic radicals produced in ionized environments²⁹ and subsequent exposure to ionizing radiations in the PSN³⁰

have been proposed as potential mechanisms to produce significant D enrichments in chondritic organics. For N, several models are still considered. The comparison of the N isotope compositions of inner and outer Solar System bodies indicates that isotopically processed N was already ubiquitous in the inner Solar System about 0.3 Myr after Solar System formation^{31,32}. Although self-shielding effects during the photodissociation of nebular N₂ is a viable process to produce early enrichments in the rarer ¹⁵N isotope^{33,34}, specific isotope exchange in so-called pre-dissociative states^{35,36} has been proposed to explain the isotopic ‘hotspots’ observed at the micrometre-scale in chondritic organics (for example, δ¹⁵N up to about 4,500‰ (refs. 37,38)). The ¹³C enrichments in C-rich grains, with respect to CO, may also be attributed to photodissociation and self-shielding (Box 1) in the PSN³⁹.

In summary, isotopic variations of H, C, N and O across the Solar System hold the key to understanding the processes that controlled the distribution of life-forming volatile elements from the molecular cloud to the PSN. Yet, the respective contributions of isotopically heavy ice and organic inheritance from the interstellar medium and photochemical reactions in the PSN required to explain the large isotopic diversity currently observed in chondrites remain open to investigation. In addition, the chemical, structural and isotopic diversity of macromolecular organic materials in primitive chondrites (for example, ref. 25) suggest that secondary processes, such as aqueous and thermal alteration, contributed to produce and/or modify organic materials found today in asteroidal matter. In the following section, we discuss the distribution and evolution of Solar System volatiles in light of the physicochemical and dynamical evolution of the PSN.

Volatile diversity in early Solar System

The distribution of various H, C and N carrier phases—mainly ices and organics, together with a few additional ‘exotic’ phases such as nitride, carbide and graphite—in the early Solar System was mainly controlled by the physicochemical conditions of the PSN. Temperature played the most important role in the formation and distribution of volatile-bearing phases throughout the PSN. Broadly, it decreases with distance from the Sun (heliocentric distance) and with distance away from the disk midplane, where attenuation of solar irradiation is minimal compared with the central plane of the disk⁴⁰. The heliocentric distance at which temperatures were low enough (that is, ≤150–170 K) for water ice to condense and become incorporated into growing planetesimals is referred to as the water ‘snow line’^{20,41} (Fig. 1). A similar situation existed for complex organic materials that, owing to their generally more refractory nature, were stable at much higher temperatures (that is, >350–450 K (ref. 42)). The barrier beyond which refractory organics were stable but water existed in vapour form is known as the ‘tar line’⁴³ (Fig. 1). Sunwards of the tar line, evaporation of the least refractory organics could have locally enhanced the C/O ratio of the gas phase and induced reducing conditions⁴⁴. In this environment, organic materials and reduced phases such as nitrides and graphite constituted a potential source of volatile elements for planetesimals that formed within the ‘ice free’ region of the inner Solar System^{43,45,46}. Overall, the inner regions of the PSN were dominated by hot and reducing conditions, whereas colder, more oxidizing environments prevailed within the outer regions of the PSN²⁰. Temperature, as well as redox conditions, governed the stability of H, C and N carrier phases and ultimately the efficiency of volatile accretion on planetary bodies.

Our understanding of how small solid grains transitioned to the first planetary bodies has improved markedly over recent decades. Initially, the motion of small dust particles would have been tightly coupled to the turbulence of the gas^{41,47–49}, until they reached a sufficient size to decouple from the motion of the gas, settle in the midplane of the disk and begin radially drifting towards the central star^{50,51} (Fig. 1). The presence of ice and organic materials on the surface of dust particles may have enhanced sticking probabilities, therefore overcoming the so-called bouncing barrier^{52–54}. This process would have resulted in the

Box 1

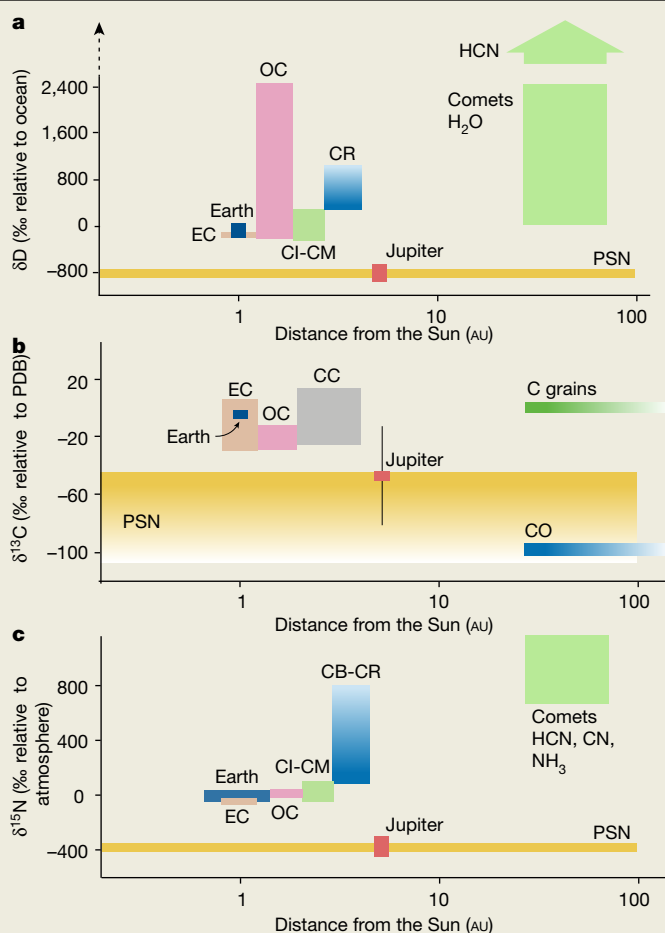
H, C and N isotope variations in the Solar System

The figure shows the H, C and N isotopic variations in the Solar System as a function of radial distance from the Sun (AU). The delta notation (δ) represents isotopic deviations of an isotopic ratio (R) relative to a terrestrial standard (R_{standard}) in parts per mil (‰):

$$\delta^j X = \left[\left(\frac{R_{\text{sample}}}{R_{\text{standard}}} \right) - 1 \right] \times 10,000.$$

By convention, the rare and heavy isotopes (^2H (D), ^{13}C and ^{15}N) are normalized to a corresponding abundant isotope (^1H , ^{12}C and ^{14}N , respectively). Positive δ values indicate that the sample is enriched in the heavy isotope compared with terrestrial standards. The different chondrite classes (enstatite chondrites (EC), ordinary chondrites (OC), and CI-CM-, CB- and CR-type carbonaceous chondrites (CC)) represent distinct meteorite parent bodies that accreted at different times and locations in the PSN¹⁴⁴. With the exception of H isotopes in ordinary chondrites¹⁴⁵, material from the outer Solar System (that is, beyond the orbit of Jupiter, at 4 AU), such as comets, generally shows more drastic heavy-isotope enrichments relative to the inner Solar System and the PSN. The meteorite data compilation is available at <https://doi.org/10.24396/ORDAR-66>. For chondrites, bulk values are given as chondrites are composed of complex mixtures of several organic and mineral components, whose isotopic composition cannot be easily estimated.

Panel **a** shows δD , where the standard is the D/H of ocean water hydrogen. Jupiter's atmosphere has a δD (ref. ¹⁴⁶) similar to the PSN¹⁴⁷. The cometary data are from ref. ¹⁴⁸ and references therein. Panel **b** shows $\delta^{13}\text{C}$, where the standard is the $^{13}\text{C}/^{12}\text{C}$ of terrestrial carbonate (Pee Dee Belemnite (PDB)). The PSN value is from ref. ³⁹. The planetary data are from a compilation by refs. ^{39,149}. These authors inferred that C in the Solar System is an isotopic mixture of C-rich grains enriched in ^{13}C and CO depleted in ^{13}C . Although $\delta^{13}\text{C}$ values have been measured for comets (for example, $65 \pm 51\%$ for CO_2 in the coma of comet 67P/Churyumov-Gerasimenko¹⁵⁰), the large associated uncertainties do not allow clear comparison with other planetary objects. The vertical black line associated with Jupiter reflects measurement uncertainty. Panel **c** shows $\delta^{15}\text{N}$, where the standard is the $^{15}\text{N}/^{14}\text{N}$ of the terrestrial atmosphere. Jupiter's



atmosphere¹⁵¹ has a $\delta^{15}\text{N}$ similar to the PSN^{152,153}. Other planetary bodies are rich in ^{15}N , including inner planets, meteorite parent bodies and comets (see ref. ¹⁵⁴ and references therein).

efficient coagulation of dust particles into decimetre-sized objects, leading to the efficient incorporation of H-, C- and N-bearing phases into planetary building blocks.

The continued growth of particles encounters a bottleneck when they reach around 1 m in diameter. This occurs as the radial drift of the larger particles towards the central star is enhanced to a point where they fall into the star faster than they can grow to larger sizes⁵¹. This barrier may be overcome by the generation of turbulence in the disk, which can create transient gas density fluctuations that push particles towards pressure maxima⁵⁰. Several models of gas flow instability have been proposed to greatly enhance particle agglomeration in association with local pressure maxima and limit inwards drifting, including so-called streaming instabilities^{55,56}. Additional 'instabilities' potentially triggering planetesimal accretion could have been generated by pressure bumps associated with important condensation fronts in the disk, such as the silicate sublimation line and the water and CO snow lines^{57,58}. Localized build-up of particles at these condensation fronts can result in the triggering of planetesimal formation⁵⁷⁻⁵⁹. The formation of planetesimals at different^{58,59}, or wandering⁶⁰, condensation fronts can have an important role in controlling the volatile budget of early planetary bodies. For example, bodies that formed at the silicate

sublimation line close to the Sun, as proposed for the terrestrial inner planets, would probably have accreted free of water ice⁵⁸.

The parent bodies of chondritic meteorites are likely to have formed at some of these local accretion zones. The so-called enstatite chondrites (EC) are made of reduced phases containing little hydrogen⁶¹ but significant C and N²⁵, suggesting their formation inside the snow line under reducing conditions. By contrast, carbonaceous chondrites (CC) contain both hydrated silicates and abundant organics, in line with their formation beyond the snow line. Ordinary chondrites (OC) have volatile contents intermediate between EC and CC, consistent with the general increase of volatile abundance and oxidation state from enstatite chondrites to ordinary chondrites (both being referred to as non-carbonaceous chondrites, or NC), and finally to carbonaceous chondrites (CC) (Box 2). The current paradigm is that NC-type and CC-type meteorites sample parent bodies presumably accreted in the inner and outer Solar System, respectively (Box 2). It is noteworthy however, that the accretion locations (that is, heliocentric distance) of the parent bodies sampled by different chondrite classes and groups are still poorly constrained and so the possibility for carbonaceous chondrites to have accreted within the orbit of Jupiter cannot be categorically excluded (for example, refs. ^{25,62}). Another important caveat

Box 2

The absence of an NC–CC dichotomy for H, C and N

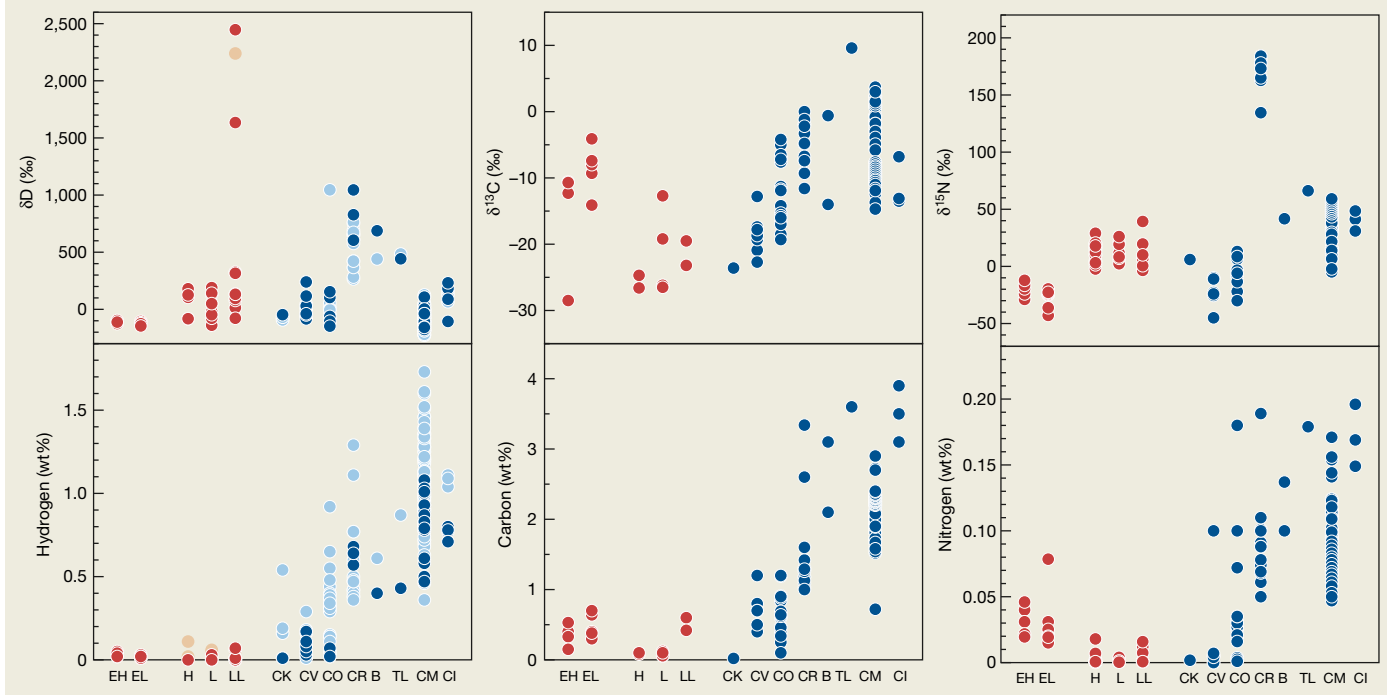
H–C–N isotope ratios and concentrations in chondrites.

Non-carbonaceous chondrites, that is enstatite (EH and EL) and ordinary (H, L and LL) chondrites, are represented in red, whereas carbonaceous chondrites (CK, CV, CO, CR, the ungrouped Bells (B) and Tagish Lake (TL), CM and CI) are represented in blue. Hydrogen abundances and δD values of meteorite samples that were degassed at temperatures between 120 °C and 200 °C before analysis to minimize atmospheric contamination⁶³ are indicated in darker blue. Note the change of vertical scale for the different sub-panels. The data shown here are summarized and tabulated in our data compilation at <https://doi.org/10.24396/ORDAR-66>.

Carbonaceous (CC) and non-carbonaceous meteorites (NC) record an isotopic dichotomy for neutron-rich isotopes, such as ⁵⁴Cr (ref. ¹⁵⁵) or ⁵⁰Ti (ref. ¹⁵⁶), which indicates that their parent bodies accreted in two isotopically distinct reservoirs, which were presumably located sunwards (NC) and beyond (CC) the orbit of Jupiter, and remained isolated from each other between about 1 Myr and about 4 Myr (for example, refs. ^{157,158}). The appearance and preservation of the NC and CC reservoirs could be related to the early formation of a massive proto-Jupiter^{157–159}, the presence of

long-lived pressure maxima in the PSN gas structure^{59,160}, or the thermal evolution of the PSN and migration of the snow line¹⁶⁰. Then, CC planetesimals from beyond Jupiter could have been implanted into the inner Solar System and the asteroid belt owing to the growth of the giant planets and/or their dynamical evolution (for example, inwards migration^{84,103}).

Whereas NC and CC chondrites (that is, primitive meteorites) can clearly be distinguished based on their distinct nucleosynthetic isotope signatures, a complex picture emerges when their H–C–N isotope compositions and abundances are compared (Box Fig. 2). Instead of displaying a clear dichotomy, there is an overall trend of increasing H, C and N concentrations from enstatite, to ordinary and carbonaceous chondrites. Isotope ratios (δD , $\delta^{13}C$ and $\delta^{15}N$) largely overlap between the NC and CC reservoirs, and between the various chondrite classes and groups, with only a few carbonaceous chondrites being significantly enriched in D and ¹⁵N. Consequently, the NC–CC dichotomy cannot be extended to the H–C–N systematics of chondrites, and not all carbonaceous chondrites can be characterized as being consistently ‘volatile rich’ compared with NC-type chondrites.



is that, although they are our best witnesses of solid materials in the PSN, chondrites have been submitted to variable degrees of radioactive and impact-induced heating. The intensity of heating is likely to have varied among chondrite groups, hence resulting in varying degrees of volatile loss^{62,63} and isotope fractionation⁶ that could mask primordial signatures. Thus, it is unclear whether the volatile content and isotope composition of a given chondrite group faithfully represents the composition of the region of the disk from which its parent body(ies) accreted.

Gradients in temperature, redox state and physicochemical conditions of the PSN undoubtedly had a significant role in distributing volatiles throughout the Solar System, resulting in the most volatile-rich planetesimals being formed in the cold, outer Solar System (Box 2). In the following sections, we discuss the possibility that material from

the outer Solar System provided the inner planets with water, pointing to a complex origin of volatiles on the terrestrial planets.

Volatile evolution during accretion

The mechanisms through which early planetesimals grew from 100-km-sized objects into fully formed planetary bodies had a major impact on how, and from where, planets were able to accrete volatiles. The classical planet-formation scenario proposes that planets grew from collisions between kilometre-sized to hundreds-of-kilometre-sized planetesimals^{64,65}. However, the formation of gas and ice giants within a classical regime of planetary formation requires a very high local density of planetesimals to build planets of several Earth masses, as has

been suggested for the core of Jupiter⁶⁶. An alternative model called ‘pebble accretion’ is therefore considered to be an important process in the formation of the giant planets, but its role in forming the terrestrial planets is unknown⁵⁶. These two models form planets over different timescales (hundreds of thousands to millions of years for pebble accretion and millions to tens of millions of years for the classical model) and across distinct feeding zones (oligarchic growth of inner Solar System planetesimals versus flux of pebbles from the outer Solar System for the classical and pebble accretion models, respectively). As such volatiles accreted to planetary bodies formed by these two mechanisms may have contrasting origins.

Planetary formation by pebble accretion can occur only within the lifetime of the PSN, which is considered to have dispersed about 4 Myr after the formation of calcium–aluminium-rich inclusions⁶⁷. The isotopic composition of the gas giant atmospheres as represented by Jupiter and Saturn are remarkably similar to the composition of the Sun (Box 1). This indicates that the gas giants captured their massive atmospheres within the lifetime of the PSN, which is most compatible with pebble accretion processes^{68,69}. The early accretion of planetary bodies is further supported by the presence of iron meteorites originating from cores of disrupted planetesimals that had experienced planetary differentiation within the first millions of years of PSN evolution (for example, refs. 70,71). In this framework, it is possible that some of the terrestrial planets also grew rapidly, potentially by pebble accretion, within the lifetime of the PSN. Estimates on the age of core formation on Mars based on ¹⁸²Hf–¹⁸²W (where extinct ¹⁸²Hf decayed to ¹⁸²W with a half-life of 9 Myr) measurements of Martian meteorites and estimates for the elemental Martian hafnium (Hf)/tungsten (W) ratio indeed suggest that Mars reached half of its current mass in less than 3 Myr (ref. 72).

A consequence of early and rapid accretion is that some planetary bodies would have formed within the lifetime of the short-lived radioisotope ²⁶Al, that is, less than 2 Myr after Solar System formation. Heat generated from the decay of ²⁶Al would probably have induced melting and the formation of a magma ocean, resulting in significant loss of planetary volatiles owing to degassing. The analysis of achondrites, representing the remnants of the earliest planetary crusts crystallized from a magma ocean, indicates depletion of primordial chondritic noble gases⁷³, confirming that significant volatile loss occurred on early planetary bodies. Hence, the presence of magma oceans on the early planets probably left their interiors depleted in volatiles⁷⁴. Larger planetary embryos (>10% the mass of Earth, M_E , about 6×10^{24} kg) may have been able to retain part of the degassed volatiles within their tenuous atmospheres. Furthermore, if they grew to sufficient size within the lifetime of the PSN, then they could have directly accreted volatiles by gravitationally capturing nebular gas. In-gassing of a dense gravitationally captured atmosphere into the mantle during periods of magma ocean could have resulted in the preservation of volatiles deep within the planetary mantles⁷⁵.

On Earth, where we have direct access to mantle-derived samples, it has been possible to determine the isotopic composition of mantle helium (He) and neon (Ne) (the two most abundant noble gases in the PSN). So far, the maximum measured ²⁰Ne/²²Ne ratio in deep-mantle-derived samples is about 13.0 (refs. 76,77). This value is notably higher than the range observed in chondrites (8.2–12.7), suggesting that Earth acquired volatiles from in-gassing of gravitationally captured PSN gas (solar ²⁰Ne/²²Ne = 13.36 ± 0.18 (ref. 78)) during episode(s) of magma ocean^{76,77}. The ²⁰Ne/²²Ne isotope of the upper mantle, is however within the range of the solar wind irradiated particles (<12.7) found in chondrites, indicating that Earth continued to accrete He and Ne from chondritic sources following the dispersion of the PSN⁷⁹. In contrast to He and Ne, the krypton (Kr) and xenon (Xe) isotopic signatures of both the upper and the lower mantle are dominated by what appears to be a carbonaceous chondritic component^{80–82}. This dichotomy in the origin of the light and heavy noble gases could be due to the relatively lower concentrations of Kr and Xe in the PSN, which, coupled with their lower solubility and diffusivity in magma oceans⁸³, would result in Kr

and Xe being far less efficiently in-gassed than He and Ne⁷⁵. The mantle noble gas record therefore requires that (1) terrestrial planets grew to a significant fraction of their present-day masses within the lifetime of the PSN, and (2) outer Solar System material contributed to the accretion of early Earth either through the influx of pebbles from the outer Solar System⁵⁶ or the early injection of outer Solar System planetary bodies to the inner Solar System during giant planet migration⁸⁴.

Given that the H, C and N isotope compositions of the bulk silicate Earth (BSE) are clearly distinct from the PSN (Box 1), any PSN contribution to the major terrestrial volatiles must have been limited. Unlike the inert noble gases, the behaviour of H, C and N during silicate melting and degassing greatly depends on redox conditions and speciation^{85,86}. Under reducing conditions (with oxygen fugacity similar to that of enstatite chondrites⁸⁷), C and N would be predominantly contained in reduced phases such as graphite, carbides and nitrides⁸⁸, which could be preserved in the mantle during episodes of magma ocean⁸⁶. Hence, a fraction of the original C and N accreted to terrestrial planets could have been preserved within magma oceans and degassed later to form planetary atmospheres if the planets became more oxidizing⁸⁹. On the basis of the isotopic similarities (titanium, chromium, nickel, oxygen and so on) between enstatite chondrites and Earth, it has been suggested that they accreted from a common reservoir in the inner Solar System^{90,91}. Interestingly, the $\delta^{15}\text{N}$ of Earth’s mantle measured within deep-mantle diamonds is indeed most similar to that of enstatite chondrites^{92,93}, suggesting that mantle volatiles may record the earliest phases of terrestrial accretion from an enstatite chondrite-like source⁶¹ (Box 3). Although nebular in-gassing may have been a major source of He and Ne in Earth’s mantle, it does not appear to have been a major contributor of C and N to terrestrial planets.

As H is the major constituent of the PSN, any input to Earth’s mantle via in-gassing could potentially supply several oceans worth of equivalent water⁷⁵. Analyses of mantle-derived samples with high ³He/⁴He ratios, thought to sample a primordial mantle reservoir containing solar He and Ne, have yielded δD values from –218‰ (ref. 94) to –75‰ (ref. 95). The highly negative δD values have been taken as evidence for the potential presence of a solar H component ($\delta\text{D} = -800\text{‰}$; Box 1) in the deep mantle. Alternatively, δD in the some of the most primitive mantle-derived samples are in line with measurements of enstatite chondrites⁶¹ (Box 3), again suggesting that the early Earth was potentially retentive to volatiles delivered from some of the earliest accreted solid materials. The presence of PSN hydrogen in the terrestrial mantle and potential implications for the origin of terrestrial water therefore remain ambiguous.

Finally, a significant fraction of C⁹⁶, N^{85,97}, H^{98,99} and noble gases¹⁰⁰ could have been incorporated into planetary cores during differentiation. The volatile element content of the terrestrial core and the core’s potential role in modulating the volatile content and isotopic compositions of Earth’s mantle, are largely unknown. As shown in Fig. 2, the BSE is depleted in C, N and H relative to the most pristine chondrites. This implies that if Earth or its planetary precursors comprised an appreciable fraction of chondritic material, then a significant amount of these elements must have been lost to space and/or segregated into a hidden terrestrial reservoir such as the core. Given these uncertainties, isotopic tracers (for example, nucleosynthetic anomalies) are often regarded as being more compelling than elemental abundance ratios to address the origin of terrestrial planetary building blocks (Box 3).

Terminal stages of volatile accretion

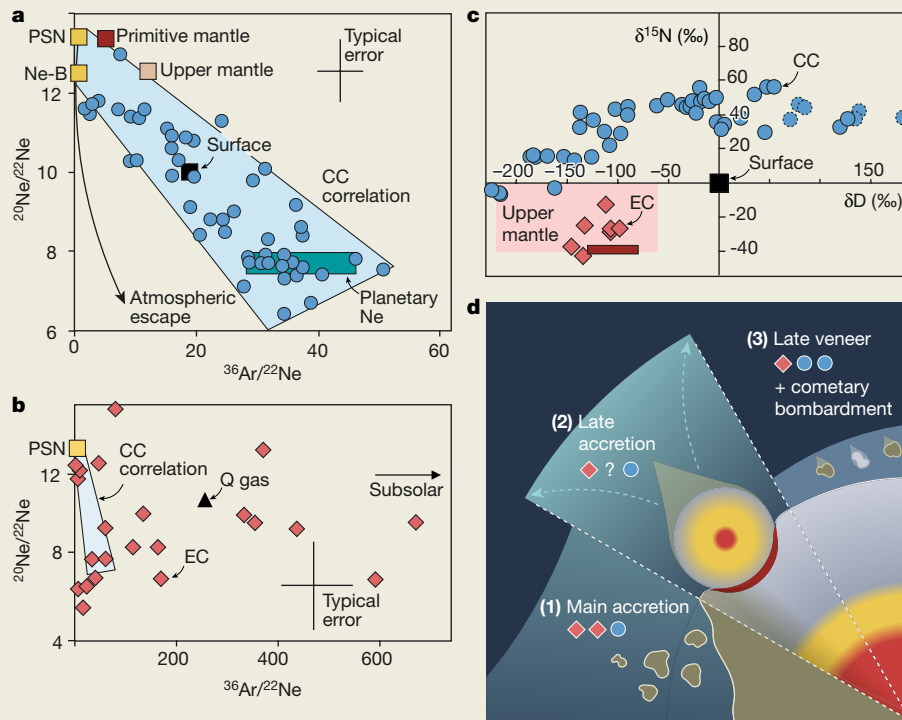
Although Earth probably formed predominantly from NC-type material sourced locally from the inner Solar System⁹¹, CC-type materials comprised a non-negligible fraction of Earth’s accretion¹⁰¹. Combining isotope systematics of elements with distinct geochemical affinities, it is possible to constrain the origin of terrestrial building blocks for different stages of Earth’s formation⁹¹. Siderophile elements (that is, metal-loving elements such as nickel and molybdenum) found within the present-day mantle are likely to record the later stages of accretion (10–20% of Earth’s

Box 3

A genetic link between chondritic and terrestrial (mantle and atmosphere) volatile reservoirs

Here we compare the Ne, N and H isotope and noble gas elemental ratios of enstatite chondrites and carbonaceous chondrites with terrestrial reservoirs. In the $^{20}\text{Ne}/^{22}\text{Ne}$ versus $^{36}\text{Ar}/^{22}\text{Ne}$ space, noble gases in the terrestrial atmosphere and oceans ('surface') fall along the CC correlation (represented here by CI and CM chondrites), strongly suggesting a CC-like origin for terrestrial volatiles at Earth's surface⁷ (panel **a**). 'Planetary Ne' is an end-member composition (defined by ref. ¹⁶¹) from carbonaceous chondrites. This composition represents a mixture of different presolar grains¹⁶². Isotopic and elemental fractionation driven by atmospheric escape to space (curved arrow) cannot account for the composition of atmospheric noble gases, as otherwise proposed^{117,163}. The range of noble gas signatures in EC is distinct from the CC trend (panel **b**) suggesting that they are unlikely to account for the atmospheric composition. Noble gases in EC are enriched in ^{36}Ar compared with CC, owing to a greater relative contribution from insoluble organic matter (labelled

Q (ref. ¹⁶⁴) and implanted solar gases ('subsolar'¹⁰⁹). Panel **c** shows that the hydrogen and nitrogen isotopic compositions of the mantle and Earth's surface are also consistent with a transition from EC- to CC-dominated accretion. Finally, a schematic diagram (panel **d**) outlines the main stages of Earth accretion (which culminated in the moon-forming impact), together with the late veneer, with an indication of the primary carriers of volatiles associated with each stage—EC (diamonds) or CC (circles) source of volatiles. References for the different chondritic and terrestrial endmembers are given in refs. ^{7,161}. Better quantification of the relative contributions of EC-type versus CC-type sources of volatile elements to Earth is, however, challenging owing to the fact that, although distinct, both types show large ranges of internal variations in their isotopic and elemental compositions (Box 2). Panels adapted with permission from: **a,b**, ref. ¹⁶⁵, Elsevier; **c**, ref. ⁶¹, AAAS.



accretion), after core formation had largely ceased. From the analysis of molybdenum isotopes in the mantle, it has been suggested that the later stages of Earth's accretion contained 30–60% CC-type material¹⁰². As CC chondrites are in general enriched in water (and in most cases C and N; Box 2) relative to NC chondrites, this high CC contribution during later accretion—potentially associated with the Moon-forming impact—could have supplied Earth with a considerable proportion of its volatile budget. This transition towards a higher CC contribution in the later stages of accretion appears to be further substantiated by the difference in volatile composition between Earth's mantle (early arriving) and surface reservoirs (late arriving) (Box 3). The reason for the apparent transition towards increasing CC contributions to Earth's accretionary material is unknown but may be related to the continual input of outer Solar System material

either by the inwards drift of pebbles or the injection of planetary bodies during migration of the gas giants^{84,103} (Box 2).

The late stages of planetary formation via planetesimal accretion would have had significant consequences for the delivery and retention of volatile elements on the inner planets. First, colliding planetesimals may have been differentiated, hence exhibiting significant fractionation of volatiles between their surface, mantle and core¹⁰⁴. Carbon is generally more siderophile in nature than N (and so more efficiently sequestered to the core of differentiating planets^{85,105}), resulting in a sub-chondritic C/N in the bulk silicate portion of planetary bodies. Yet, the BSE is characterized by a super-chondritic C/N ratio^{10,106} (Fig. 2), suggesting that chondritic accretion followed by differentiation cannot explain this ratio. As C may become less siderophile than N in sulfur (S)-rich alloys, one possibility is that Earth inherited most of its C

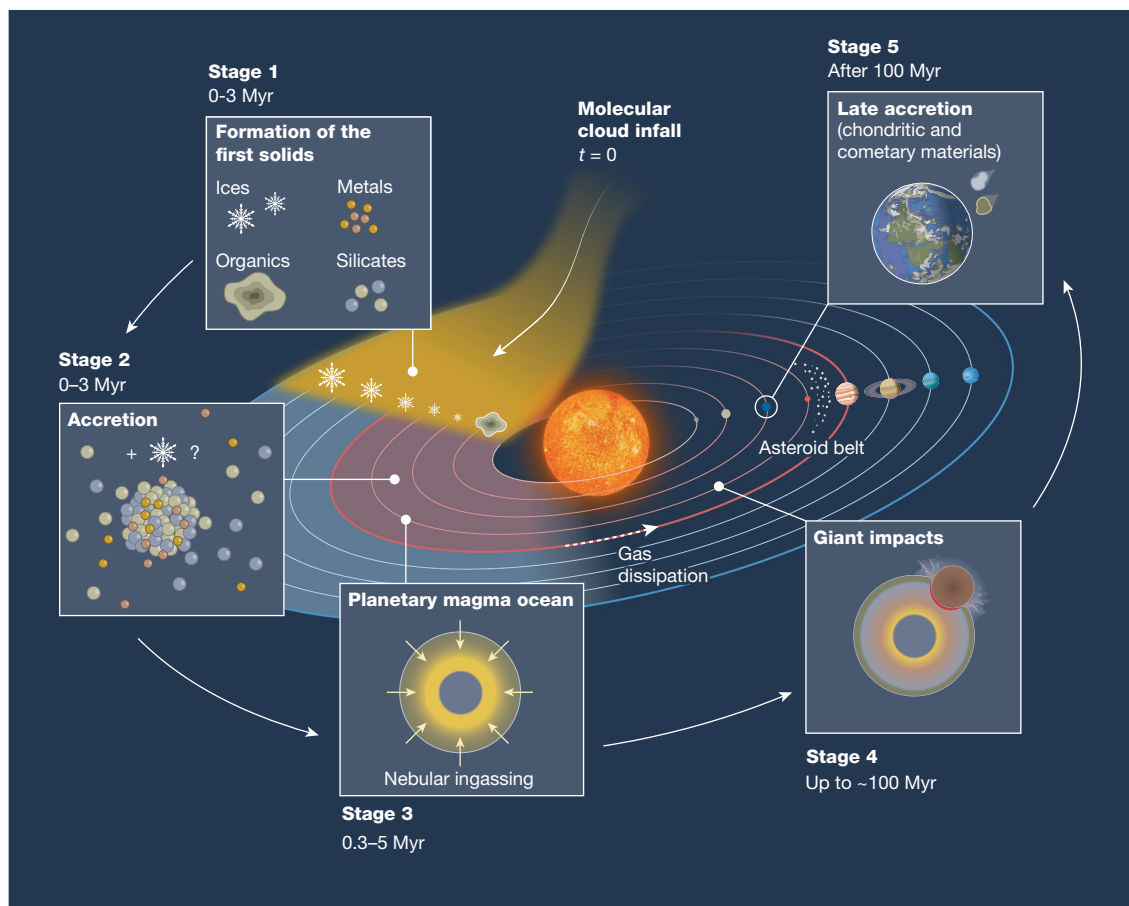


Fig. 3 | Main stages of planetary formation and volatile incorporation into terrestrial building blocks within the PSN. Although part of the molecular cloud matter could have been delivered to the protoplanetary disk and incorporated into planetary bodies (for example, comets) with little to no modification, the vast majority of the H-, C- and N-bearing molecules from the molecular cloud would have been destroyed (vaporized) en route to the disk via thermal and stellar ultraviolet processing¹⁹. Stage 1: formation of the first solids via condensation of silicates and ice, and polymerization of organic materials.

and N from a S-rich differentiated planetary body with a super-chondritic C/N⁸⁶. Alternatively, if N was preferentially released to the early atmosphere relative to C, then early episodes of impact-driven atmospheric escape could have induced preferential loss of N, hence raising the bulk C/N of Earth¹⁰⁷. Notably, the record of atmospheric loss during episodes of giant impacts may be reflected in the He/Ne of Earth's mantle¹⁰⁸. During giant impacts, the preferential degassing of less soluble Ne would increase the ³He/²²Ne in the mantle residue. Raising the ³He/²²Ne of the upper mantle from a solar or chondritic value of about 2 to its modern day value of about 10 would require at least two episodes of magma ocean formation and atmospheric loss¹⁰⁸.

The main accretion phase of Earth ended with the Moon-forming impact¹⁰⁹, which set the stage for the subsequent evolution of our planet towards a habitable world^{110,111}. The high angular momentum of the Earth–Moon system calls for an extremely energetic event, which probably resulted in the partial, or complete, melting of the proto-Earth^{112–114}. To what extent terrestrial volatiles contained within the fledgling ocean and atmosphere survived this event is a matter of debate^{115,116}. A dramatic loss of atmospheric volatiles during the Moon-forming event is however supported by the observation that our planet as a whole contains at most a few per cent of ¹²⁹Xe initially produced from the decay of short-lived ¹²⁹I (half-life 15.6 Myr)^{115,117,118}, indicating that up to 99% of terrestrial ¹²⁹Xe (and presumably other volatile elements to varying degrees) was lost during giant impacts akin to the Moon-forming event.

Stage 2: early accretion of the first planetary objects by accumulation of variable amounts of silicates, organics and ice. Stage 3: planetary bodies that reach a sufficient size to capture nebular atmospheres may experience episodes of nebular in-gassing during periods of magma oceans. Stage 4: after dissipation of the PSN gas, planetary embryos may collide during giant impacts, such as the one that formed the Moon. Stage 5: after Moon formation, Earth experienced late episodes of chondritic material accretion (referred to as the late veneer), accompanied by marginal contributions from comets.

Evidence for accretion following the Moon-forming impact arises from the composition of highly siderophile elements (rhenium, osmium, iridium, ruthenium, platinum, rhodium, gold and palladium) in the mantle. These elements, which concentrate into metal phases, and hence the core, during planetary differentiation, are found in excess in the terrestrial mantle relative to the expected amounts given their wholesale removal to the core. Furthermore, the relative proportions of these elements are comparable to that of chondrites, indicating that an addition of about 0.5 wt% M_E of chondritic material to a mantle that was barren in highly siderophile elements occurred after core formation^{119–121}. From mass-balance considerations, ref. ¹²² proposed that a roughly 0.5 wt% M_E 'late veneer' consisting of CC-type material would yield enough H₂O and C to form the surface reservoir of our planet, yet provide too much atmospheric noble gases by a factor of 3–5. It is noteworthy that estimates of mantle water contents range from one¹²³ to up to five to ten ocean masses⁷. This illustrates how poorly constrained H, C and N abundances for the BSE are, even more so considering the potential volatile budget of the terrestrial core^{85,86,105,124,125}. However, it is clear that volatile elements added after the Moon-forming event cannot account for the whole BSE inventory, hence requiring a significant fraction of terrestrial volatiles to have survived the main stages of terrestrial formation, including giant impacts.

Finally, comets that are rich in water ice (10–50%) and organic materials¹²⁶ have long been proposed as potential suppliers of water and

biologically relevant molecules to early Earth¹²⁷. Importantly, the D/H of cometary water ice is generally—but not always¹²⁸—higher than the terrestrial ocean value. However, one important finding from the recent Rosetta mission led by the European Space Agency was that the Xe isotope composition of comet 67P/Churyumov–Gerasimenko exhibits a drastic depletion in the two heaviest isotopes (^{134,136}Xe), a feature that had long been recognized in the terrestrial atmosphere¹¹⁷ but had remained unexplained. On the basis of a binary mixing model between cometary and chondritic components, the cometary contribution to atmospheric Kr and Xe was estimated to be 20 ± 5% (refs. ^{129,130}), which equates to comets contributing ≤1% to the terrestrial H₂O, C and N budget.

Our understanding of how volatiles accreted to planetary bodies in the inner Solar System is undoubtedly dominated by an Earth-centric view and is limited by our lack of knowledge regarding the composition of Mercury and Venus and, to a lesser extent, Mars¹³¹. One possibility is that Venus, Earth and Mars formed from a comparable pool of accretionary material, implying that terrestrial planets potentially started with similar volatile contents. For Mars, there is convincing evidence that the red planet once had oceans, or at least liquid water in the distant past >3–4 Ga (ref. ¹³²), potentially rendering the planet hospitable to life. Likewise, Venus, considered to be Earth's sister planet, could have been wet in the distant past, and potentially habitable¹³³. However, both planets underwent drastically different evolution paths to Earth owing to the combination of different heliocentric locations and masses. Venus today is inhospitable, with a ground temperature of 750 K, a carbon dioxide (CO₂)-rich atmosphere 90 times as dense as Earth's, and the absence of liquid water on its surface¹³⁴. The Venusian D/H ratio measured in atmospheric sulfuric acid is much higher than that of the terrestrial oceans by a factor of 150 ± 30 (ref. ¹³⁵), suggesting that any water that may have been present on Venus was probably lost owing to photodissociation by solar ultraviolet photons and H escape to space. On Earth, a stable atmosphere^{136,137} and surficial liquid water were already present as early as 4.3–4.4 Ga (refs. ^{138,139}). The lack of significant escape of water to space resulted in a planetary surface favourable to the development of life.

Implications and future directions

The series of events that protractedly shaped Earth into a habitable world remains far from being unravelled. The complex origin of volatiles such H, C, N and O within terrestrial planets reflects the heterogeneous nature and distribution of volatile elements within their planetary building blocks, which resulted from a complex interplay of (1) heterogeneous inheritance from the parental molecular cloud, (2) photo- and physicochemical processes that occurred within the PSN, and (3) dynamical evolution of growing planetary bodies in the early Solar System. The main steps of planetary formation and pathways of volatile element incorporation into terrestrial planets are summarized in Fig. 3.

The increasingly precise analysis of the primitive matter present in the nascent Solar System on the one hand, and that of materials from the deep Earth on the other hand, make it possible to refine the genetic relations between the protoplanetary nebula and planets located in the habitable zone. In this sense, a new era of exploration of the Solar System awaits, which will soon see the exploration of the icy moons of Jupiter, which potentially contain liquid water below their surface (the European Space Agency Jupiter Icy Moons Explorer (JUICE), the NASA-led DAVINCI+ mission to analyse the composition of Venus' atmosphere, as well as asteroid sample return missions such as Hayabusa2 (returned in 2020) and OSIRIS-REx (returned in 2023)). In the coming decades, we will also have samples returned from Mars allowing us to understand its environment in key periods, which may have seen the development of oceans and, potentially, a fledgling biosphere. The study of primitive environments on worlds outside our Solar System will also be opened up in the future by the recently launched James Webb Space Telescope. This ground-breaking instrument will sniff out molecules such as carbon dioxide and water vapour in the atmospheres of exoplanets, helping scientists to understand the chances of life to develop on worlds outside our Solar System.

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