

On the Origin(s) and Evolution of Earth's Carbon

Sami Mikhail¹ and Evelyn Füri²



1811-5209/19/0015-0307\$2.50 DOI: 10.2138/gselements.15.5.307

The isotopic “flavor” of Earth’s major volatiles, including carbon, can be compared to the known reservoirs of volatiles in the solar system and so determine the source of Earth’s carbon. This requires knowing Earth’s bulk carbon isotope value, which is not straightforward to determine. During Earth’s differentiation, carbon was partitioned into the core, mantle, crust, and atmosphere. Therefore, although carbon is omnipresent within the Earth system, scientists have yet to determine its distribution and relative abundances. This article addresses what we know of the processes involved in the formation of Earth’s carbon reservoirs, and, by deduction, what we know about the possible origins of Earth’s carbon.

KEYWORDS: cosmochemistry, carbon isotope geochemistry, meteoritics, planetary science

INTRODUCTION

Earth is unique among the planets in our solar system in that it has liquid water at its surface, it has fostered life, and it has active plate tectonics. Whether these phenomena are linked remains one of the most exciting puzzles in planetary science and is central to the search for habitable exo-worlds. Earth’s clement environment is related to its atmospheric chemistry, which is warm enough to stabilize liquid water at its surface but cold enough to permit plate tectonics (Foley 2015). To understand the chemistry of Earth’s initial atmosphere and how this developed into a habitable environment, we must know the origins of Earth’s carbon.

An important tool for solving for the origin of Earth’s volatiles comes from the stable isotopes of carbon, ^{12}C and ^{13}C (Fig. 1), complemented with other isotope systems (e.g., hydrogen, nitrogen, noble gases) (Grady and Wright 2003; Füre and Marty 2015; Marty et al. 2016; Alexander et al. 2017). The carbon isotope signatures of the different solar system objects are strikingly homogeneous (Woods and Willacy 2009) and overlap with the average carbon isotopic value of Earth’s convecting upper mantle (i.e., average $\delta^{13}\text{C} \approx -5\text{‰}$)

(Deines 2002). Multi-element isotope datasets allow scientists to record the isotopic “flavor” of the loosely grouped “volatile elements” as a function of reservoir type. This permits the identification of primordial reservoirs (e.g., solar nebula gas, asteroids, and comets), and it allows us to decipher the cosmic provenance of terrestrial volatiles, including carbon. We can then compare the isotopic signatures of these reservoirs to what we know of Earth and so identify the proportions of the components that make up Earth’s carbonaceous cocktail.

A major caveat is that, throughout Earth’s history, this cocktail has been shaken and stirred by planet-defining events such as differentiation (i.e., core formation), the “giant” Moon-forming impact, and the proposed “late veneer”. As a result, constraining the origin, abundance, and distribution of carbon in the Earth system is not a simple task. Importantly, carbon forms various compounds with many other elements. This means that carbon can, under the right conditions, follow the pathway of the atmophile, lithophile, siderophile, and (very rarely) the chalcophile elements (see TABLE 1). As a consequence,

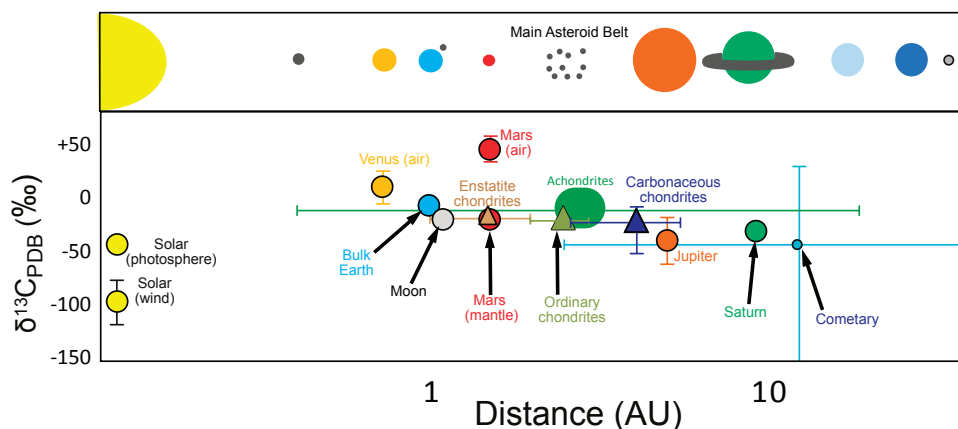


FIGURE 1 (TOP) The broad architecture of the solar system showing the Sun, 8 planets, asteroid belt, and the dwarf planet Pluto. (BOTTOM) The measured carbon isotope values expressed as $\delta^{13}\text{C}$ for a variety of solar system objects: $\delta^{13}\text{C} = [({}^{13}\text{C}/{}^{12}\text{C})_{\text{sample}}/({}^{13}\text{C}/{}^{12}\text{C})_{\text{PDB}} - 1] \times 1000$. Abbreviation: PDB = Pee Dee belemnite standard. Error bars for $\delta^{13}\text{C}$ reflect standard deviations from the mean. The error bars for distance indicate the possible range of formation distances. Abbreviation: AU = astronomical unit (mean distance of the Earth from the Sun). DATA FROM GRADY AND WRIGHT (2003); LYONS ET AL. (2018); WOODS AND WILLACY (2009) AND REFERENCES THEREIN.

1 School of Earth and Environmental Sciences, Irvine Building University of St Andrews North Street, St. Andrews KY16 9AL, Fife, UK E-mail: sm342@st-andrews.ac.uk

2 Centre de Recherches Pétrographiques et Géochimiques, CNRS-UL 15 rue Notre Dame des Pauvres, BP20 54501 Vandœuvre-lès-Nancy, France E-mail: efueri@crpg.cnrs-nancy.fr

TABLE 1 EXAMPLES OF CARBON COMPOUNDS (AND ALLOTROPES) IN THE CONTEXT OF THE GOLDSCHMIDT CLASSIFICATION.

Group	Example carbon compound
Atmophile	Carbon dioxide (CO ₂ gas)
Lithophile	Magnesite (MgCO ₃)
Chalcophile	Carbon monosulfide (CS)
Siderophile	Cohenite ([Fe,Ni,Co] ₃ C)
Inert	Diamond/Graphite

carbon is incorporated into every layer of the Earth system (Kelemen and Manning 2015). Thus, although carbon is usually grouped as a highly volatile element (alongside hydrogen, the noble gases, the halogens, and nitrogen), the notion that there has been a considerable loss of carbon during planetary accretion and differentiation is potentially inaccurate. The concept of volatility during condensation and evaporation is not directly applicable to the geochemistry of carbon *per se*. This is because carbon is rarely found solely in its native state (i.e., graphite, diamond, or amorphous). Instead, carbon exists in a variety of materials with different oxidation states (i.e., compounds) that have vastly different physical and chemical properties, such as their boiling points (Fig. 2). Thus, one must be aware that stating a particular volatility value for carbon is inherently inaccurate. Instead, it is more useful to consider the relative volatilities of specific carbonaceous compounds. For example, methane is a highly volatile compound (similar in volatility to argon), which only exists in solid form in the colder regions of the outer solar system, whereas graphite and diamond are the least volatile (most refractory) naturally occurring inorganic carbonaceous materials (Fig. 2) and were preserved in the inner planet-forming region of the solar system.

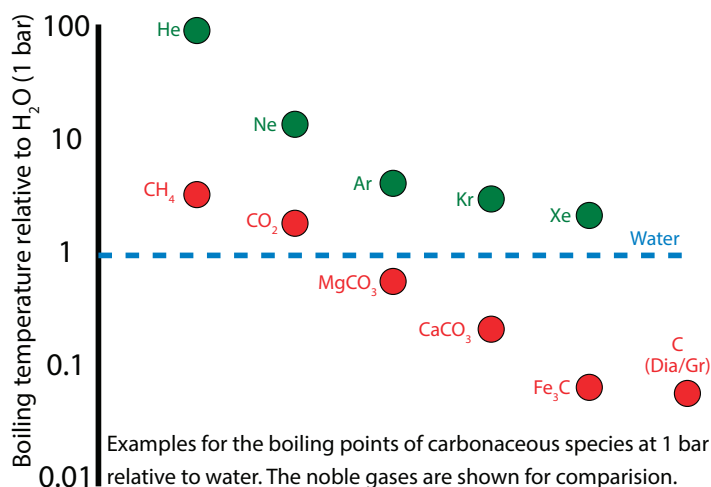


FIGURE 2 The boiling (CH₄, CO₂), decomposition (MgCO₃, CaCO₃), and melting (Fe₃C, C) temperatures (i.e., volatilities) for various carbon species and noble gases relative to water at 1 bar. This figure illustrates the concept of volatile retention and loss during planetesimal differentiation and degassing. The states of matter are temperature and pressure dependant. We show these examples, relative to water, for a range of carbon species and the noble gases to make clear that carbonaceous material has no single boiling, decomposition, or melting point and can be described from highly volatile (CH₄) to very refractory (Dia/Gr). Note that not all of these species were necessarily present during the degassing of planetesimals or planets, or during the formation of chondrites. Abbreviations: Dia = diamond; Gr = graphite.

This article provides an overview of the pathways followed by carbon in the solar nebula and during the accretion and evolution of planetesimals and planets, including the formation of the Earth–Moon system. We also outline what we know of the origin(s) of Earth’s carbon, including how the bulk terrestrial carbon isotope value might have been fractionated, and we highlight the need for robots to boldly go where no robots have gone before in order to address the exciting gaps in our knowledge.

CARBON IN THE SOLAR SYSTEM

The solar system formed ~4.567 billion years ago from gas and dust during the gravitational collapse of a dense core within an interstellar molecular cloud. A protoplanetary disk (traditionally referred to as the solar nebula) coalesced around the growing young Sun and had a strong thermal gradient across the disk, i.e., temperatures decreased away from the center. It was within this rotating disk that the planets formed. Carbon was present throughout this celestial system: in the hotter regions, it was in the form of gaseous CO, CO₂, and CH₄; beyond the soot line (which is mobile as a function of solar luminosity; Kress et al. 2010), it appears in admixtures of refractory organic molecules and pre-solar C-rich grains; in the cold regions, it occurs as CO-, CO₂-, and CH₄-bearing ices. Cooling led to the formation of protoplanetary dust (i.e., calcium–aluminum-rich phases and Mg-rich chondrules), followed by the accretion of undifferentiated planetesimals. We can still sample such primitive objects in the form of chondritic meteorites, some of which are carbon-rich (e.g., CI carbonaceous chondrites of the Ivuna type). The presence of a potent heat source in the form of the short-lived radionuclide ²⁶Al (with a half-life t_{1/2} ≈ 0.7 million years) meant that planetesimals that accreted within ~1 million years of solar system formation melted and differentiated (Carlson et al. 2014), creating bodies with metallic cores and silicate mantles and crusts (e.g., asteroid Vesta; Hin et al. 2017). Fragments of these cores and mantles/crusts still fall onto Earth today in the form of iron and achondritic meteorites, respectively.

On average, the achondrites contain low carbon abundances, presumably because the C-carrier phases were destroyed during high-temperature processing. However, the high-energy stages of planetesimal formation did not always entirely remove carbon from a given planetesimal. For example, meteorites from 4 Vesta typically contain 10–30 ppm carbon and have no free carbon phase, whereas ureilites—a rare type of stony (silicate-rich) meteorite—can contain up to 7 wt% carbon and have free carbon phases in the form of graphite and diamond (Grady and Wright 2003). Even iron meteorites, which represent relics of core material from differentiated bodies, show significant carbon abundances (predominantly in the form of graphite inclusions and carbides, but also as dissolved impurities in the Fe–Ni alloy) (Grady and Wright 2003), indicating that the metallic cores of planetesimals had sequestered carbon during core–mantle differentiation.

Further accretion of dust and planetesimals resulted in the formation of telluric (silicate-metal dominated) asteroids, and eventually, the rocky planets of the inner solar system. The terrestrial planets, it is worth noting, presumably formed within the mobile snowline, a virtual limit beyond which water freezes, currently situated at 2.7–3.2 AU [astronomical unit, the mean distance between the Earth and the Sun]. The equivalent also exists for carbon, i.e., refractory organic compounds are stable only beyond the soot-line (Kress et al. 2010), whereas CO, CO₂, and CH₄ ices only exist beyond the orbit of Saturn. Thus, it is considered that the planetesimals of the inner solar system were originally carbon-depleted. At greater heliocentric distances, the

process of accretion involved organic carbon-bearing ices (comet-formation), and the birth of the gas giants (Jupiter and Saturn) and ice giants (Uranus and Neptune). The result is a (semi-)stratified solar system, with rocky interior planets and gaseous/icy outer planets.

In between these two planetary families (rocky and gaseous/icy) resides an orbiting array of left-over planetary building blocks known as the asteroid belt (FIG. 1). Despite its apparently well-ordered current orbital architecture, the evolution of the solar system is thought to have been dynamic. To a first approximation, the building blocks of the terrestrial planets were depleted in elements with volatile affinities (Albarède 2009). However, volatile-rich material, isotopically akin to carbonaceous chondrites, from beyond the snow- and soot-lines, could have been scattered into the terrestrial planet forming region due to the inward and outward migration of the giant planets, as proposed in the “Grand Tack” model (Walsh et al. 2011), or simply because the orbits of nearby planetesimals were destabilized by the growth of the giant gaseous/icy planets (Raymond and Izidoro 2017).

CHONDRITIC CARBON—THE OLDEST ARCHIVE

The chondritic meteorites represent the most primitive rocks of the early solar system that can be examined in laboratories today. They are a group of metal-bearing stony objects, which agglomerated at varying distances from the Sun, and they can be divided into three major classes: carbonaceous, ordinary, and enstatite (FIG. 1). Although several groups of the class known as the carbonaceous chondrites contain a large amount of carbon (up to ~3.5 wt%) (Grady and Wright 2003), the name “carbonaceous” is somewhat misleading because some ordinary and enstatite chondrites are more carbon-rich. Most of this carbon is in the form of organic compounds dispersed within the chondritic matrix (e.g., Alexander et al. 2017), but inorganic carbon phases are also present (i.e., graphite, diamond, carbides, and carbonates). The bulk $\delta^{13}\text{C}$ value of different chondrite classes ranges from -25‰ to $+4\text{‰}$ (Grady and Wright 2003), a range that encompasses the estimates of the bulk carbon isotope value of Earth’s mantle (average $\delta^{13}\text{C} \approx -5\text{‰}$) (Deines 2002). Furthermore, the hydrogen and nitrogen isotopic signatures of CI chondrites—the richest in water, organics, and noble gases among all meteorites—closely match those of Earth (Füri and Marty 2015). This implies that the major volatile species on Earth were derived from a cosmochemical reservoir that is isotopically similar to the volatile inventory of primitive asteroids and distinct from the icy and volatile-rich cometary bodies and the initial signature of the solar nebula (Marty et al. 2016).

Although chondritic meteorites have never been heated to the point of complete melting, they have all been heated above the sublimation temperature of the most volatile elements, such as the noble gases. This explains why the Sun shows elevated primordial noble gas abundances (^{20}Ne , ^{36}Ar , ^{84}Kr , and ^{130}Xe) relative to the chondritic values (FIG. 3), but chondritic meteorites retain solar-like refractory lithophile element abundances (e.g., Mn/Mg). If one compares the abundance of the elements in chondritic meteorites with the solar photosphere (the Sun), then a 1:1 relationship is observed for most elements when normalized to silicon (FIG. 3). Importantly, according to the “chondritic Earth model” (e.g., McDonough and Sun 1995), the bulk composition of the Earth is broadly similar to that of chondritic meteorites. Thus, one can apply chondritic data to estimate the Mn/Mg ratios for the bulk Earth system, or to calculate the size of Earth’s core, where estimates using chondritic Fe/Mg ratios agree

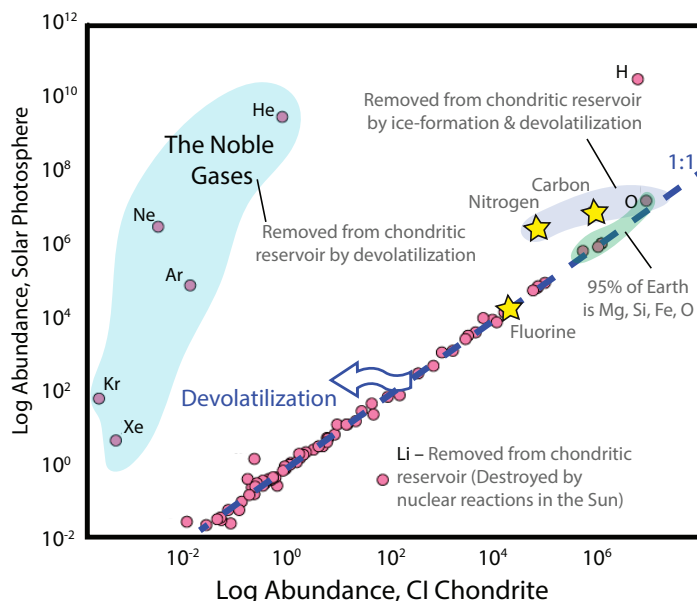


FIGURE 3 The composition of CI (carbonaceous chondrite, Ivuna type) chondritic meteorites compared to the solar photosphere where the abundances are plotted relative to one million silicon atoms. Evident in this figure is the logic behind the grouping of He, C, N, Ne, Ar, Kr, and Xe as highly volatile elements because they plot to the left of the expected nebular abundance (the 1:1 solar/chondritic ratio of the blue dashed line). Also, not all volatile elements show fractionated relative abundances, e.g., fluorine. DATA FROM LODDERS (2003) AND PORCELLI AND PEPIN (2003).

with the geophysical constraints. But one cannot use the “chondritic Earth model” to calculate the mass of carbon in the bulk Earth. Chondritic data show that carbon has been fractionated from solar nebular abundances (e.g., C/Mg), but less so than for nitrogen (e.g., N/Mg). However, both carbon and nitrogen were significantly less fractionated than the noble gases (FIG. 3). This is likely, in part, because carbon (and nitrogen) can exist in a variety of redox states with hugely variable boiling points/volatilities (see FIG. 2 for carbon). Therefore, one cannot calculate the carbon abundance for the bulk Earth using chondritic or solar data (i.e., using the C/Mg ratio). In summary, we do not know Earth’s bulk carbon abundance, but we do know that Earth’s carbon sources were fractionated from their initial abundances. In short, Earth’s C/O and C/Si ratios are certainly not solar, chondritic, nor cometary.

PLANET-DEFINING EVENTS IN THE HISTORY OF EARTH’S CARBON

Recent geochemical datasets show that Earth’s volatile elemental ratios (i.e., C/N or C/Si) are nonchondritic, suggesting that elemental fractionation occurred during planetesimal accretion (Hin et al. 2017), core formation (Dasgupta et al. 2009), giant impact(s), impact-induced atmospheric loss (Bergin et al. 2015), or a combination of all these processes (Grewal et al. 2019). Thus, long before plate tectonics began cycling and recycling Earth’s carbon between the surface and the interior, three recognized periods or events were particularly pivotal in the formation and evolution of the terrestrial carbon reservoirs. These events were either internally driven (core formation) or externally driven (the “giant” Moon-forming impact and the late veneer) (FIG. 4), and they modified the distribution of elements within planet Earth. As a result, the distribution of carbon and its isotopes between the terrestrial reservoirs—including the silicate portion that

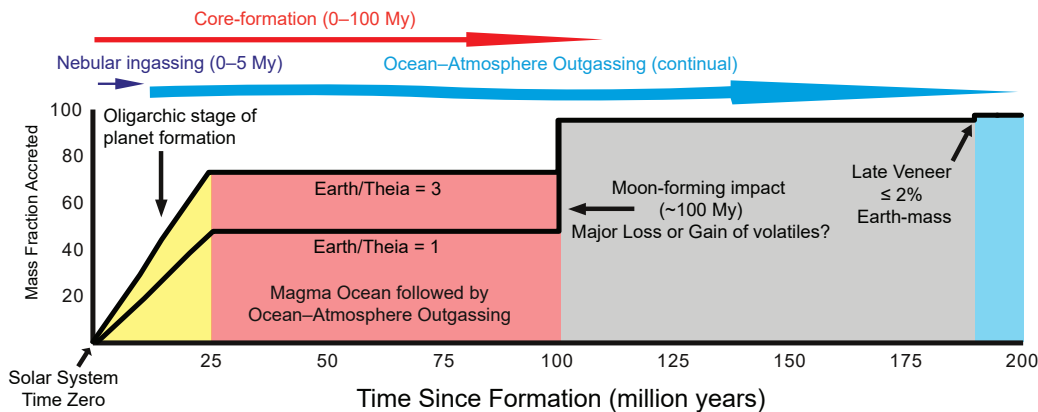


FIGURE 4 A timeline for the key events in the first 200 million years of Earth's history that could have potentially impacted on Earth's bulk carbon abundance and isotope value, as well as the carbon isotope signatures of Earth's different reservoirs/layers.

can now be sampled—has been “smudged” (more than once). Furthermore, these events may have masked the initial $\delta^{13}\text{C}$ of Earth's mantle and altered the bulk Earth carbon abundance.

Internally Driven Events

The general architecture of the Earth and the other telluric planets (having a core, mantle, crust, and atmosphere) was imposed during the earliest history of planet formation; but the composition and physical state of these reservoirs were, and are, susceptible to later modification. The large planetesimals and planetary embryos that formed within the first ~1 million years of solar system history experienced significant, and perhaps complete, melting as a result of the energy provided by kinetic and radiogenic heating (via long- and short-lived radioisotopes) (Carlson et al. 2014). Hence, the terrestrial planets and their building blocks probably experienced at least one magma-ocean stage (of unknown depth), and, upon cooling and solidification, these bodies then differentiated into a metal core, silicate mantle, crust, and a primordial atmosphere. The layering of planets is primarily imposed by density differences; but some elements (and their compounds) find their way into different layers as a function of their chemical properties (ionic charge, radius, electronegativity, and volatility). Carbon is mobile within the Earth system, where the predominant mechanisms driving exchange are diffusion, volcanism, and chemomechanical mixing (i.e., plate tectonics). Thus, Earth's carbon is in a constant state of flux operating on timescales from seconds to billions of years (Kelemen and Manning 2015). FIGURE 5 provides a snapshot of the distribution of carbon in the Earth system (today) without estimates for the size(s) of these reservoirs.

Earth's core could well be the greatest reservoir of carbon, by mass. High-pressure experiments and the presence of carbon in iron meteorites demonstrate that metal-silicate equilibration always results in some fraction of carbon partitioning into the cores of planetesimals and planets (see Wood et al. 2013). Hence, many workers have attempted to constrain exactly how much carbon could have been sequestered into the core during differentiation. There is a driving rationale for this, beyond an interest in carbon geochemistry. Geophysical data has long shown that Earth's core is a metallic alloy of Fe + ~5% Ni (McDonough and Sun 1995), but its density is too low to be simply a binary Fe-Ni alloy. To explain the density deficit requires that the core must contain 8%–12% of a component with an atomic number less than iron ($Z = 26$). Carbon has long been considered as one of the lighter elements in the core, alongside H, N, O, S, Si (Wood et al. 2013). This is important for understanding the origin of Earth's carbon if one applies a mass-balance approach because the core makes up >30% of Earth's mass. Therefore, changing the mass of carbon

in the core from a low to a high value would dramatically influence the calculated total carbon inventory of the whole planet. How much carbon is possibly stored in Earth's core strongly depends on the initial amount of carbon present in the magma ocean, as well on the metal affinity of carbon under core-forming conditions. Over the last decade, experimental studies of the carbon partitioning between Fe-Ni alloy liquid and silicate melt (e.g., Dasgupta et al. 2009; Grewal et al. 2019) have revealed that the behavior of carbon during metal-silicate equilibration is highly sensitive to the composition of the Fe-rich alloy (including the abundance of the light elements H, N, S, and Si) as well as to the pressure (depth of differentiation), temperature, and oxygen fugacity (Wood et al. 2013). Importantly, the debate currently revolves around how much carbon was sequestered into the core, and not if carbon was partitioned into the core (Dasgupta et al. 2009; Wood et al. 2013; Grewal et al. 2019). Assuming that a large amount of carbon was accreted to the young Earth and that this was then sequestered to the core, then a significant amount of the carbon now present in the terrestrial mantle must have been delivered to the Earth after core-mantle differentiation, such as by a large impactor and/or during the accretion of the late veneer.

Externally Driven Events

Planet Earth has experienced at least two stages of secondary accretion, defined as events which altered the chemistry of the bulk Earth. The first formed Earth's Moon; the second provided us with a large fraction of our precious metals (e.g., gold).

The “giant” Moon-forming impact occurred within the first 40 to 100 million years of solar system history (Carlson et al. 2014) and was a collision between the proto-Earth and a planet-sized impactor named “Theia”. The impact was so energetic that it caused the bulk silicate Earth to explode from solid rock into a vapor cloud which left a lasting geochemical fingerprint on the volatile element inventory of the Earth-Moon system (Hauri et al. 2017). However, quantifying the effect of the giant impact on carbon geochemistry remains challenging, partly because we do not know the initial or present-day carbon abundance of planet Earth. The Moon-forming impact would have resulted in the melting of most (or all) of Earth's silicate mantle in order to form a silicate vapor disc, this event being followed by the formation of a deep magma ocean (Hin et al. 2017; Grewal et al. 2019). This stage of Earth's history might have resulted in significant outgassing and the formation of a secondary atmosphere. Alternatively, Earth could have *gained* volatiles from the impactor (Grewal et al. 2019). According to the latter scenario, (partial) accretion of a large differentiated body would explain the major volatile element signature of the bulk silicate Earth. In

either case, carbon was certainly redistributed between Earth's interior and the surficial reservoirs as a result of the Moon-forming impact.

The so-termed "late veneer" was the largest meteor shower in Earth's history. This bombardment represents the final sweeping up of the residual planetesimal material following the main stage of terrestrial planet formation in the inner solar system. The late veneer hypothesis is required to explain mantle geochemistry. Importantly, the late veneer would have postdated the formation of Earth's core and the Moon-forming event and at least some stage(s) of atmosphere formation (FIG. 4). The late veneer is considered to have added the "iron-loving" highly siderophile elements (HSEs: Os, Ir, Ru, Rh, Pt, Pd, Re, Au) to the silicate Earth, and represents a contribution of ~0.1–2 wt% by mass chondritic material to Earth (e.g., Chou 1978). However, to explain what we think we know of Earth's volatile inventory (H₂O, C, N, halogens, noble gases) requires the addition of ~2 (±1) wt% carbonaceous chondrite-like matter, which is equal to or greater than the mass of material delivered by the postulated late veneer derived using HSE geochemistry (Marty et al. 2016; Alexander et al. 2017). Furthermore, recent findings on the similarity of Ru isotopic compositions of the bulk silicate Earth and of enstatite chondrites suggest that the Earth's late veneer had an enstatite chondrite-like isotopic signature. This would imply that the late veneer might have been volatile-poor (Fischer-Gödde and Kleine 2017) and that the delivery of terrestrial volatiles was not solely a late-stage event. Accordingly, Earth accreted volatile-rich material, likely sourced from beyond the orbit of Jupiter, during the main sequence of planet building. This accretion was possibly due to either lateral material transport triggered by the growth and/or migration of the giant planets during the earliest history of the solar system (Walsh et al. 2011; Raymond and Izidoro 2017) or during the giant impact phase (e.g., Grewal et al. 2019).

ASSESSING THE CARBON ISOTOPE VALUE OF THE BULK EARTH

This article began by highlighting how one can apply carbon isotope data alongside H, N, and noble gas data to constrain the origin(s) of the carbon on Earth, cosmochemically (FIG. 1). Later, we outlined several events in Earth's early history that can be described as planet-defining, such as core formation, the "giant" Moon-forming impact, and the late veneer (FIG. 4). We also noted that carbon is distributed and redistributed throughout the entire Earth system in the form of various compounds (FIG. 5).

To apply stable isotope geochemistry to trace the source of terrestrial carbon relies on the assumption that the fractionation of volatile element isotopes is negligible during processing of ice and dust in the solar nebula and throughout the accretion/differentiation stages of planetesimal and planet formation. However, and problematically, these redistribution events and processes can all impart equilibrium carbon isotope fractionation. It is now established that the degassing from magma oceans and during high-energy impact events, as observed via moderately volatile isotope systems, can result in stable isotope fractionation (Kato et al. 2015). Thus, degassing of carbon from the magma ocean of low-gravity bodies (planetesimals) could have fractionated the ¹³C/¹²C ratio of Earth's precursor material and of the young Earth itself. Early loss of carbon to space via CO₂/CO escape during degassing of a silicate magma ocean would deplete the magma ocean in the heavy isotope and decrease the ¹³C/¹²C ratio of the silicate portion of the planet (Horita and Polyakov 2015).

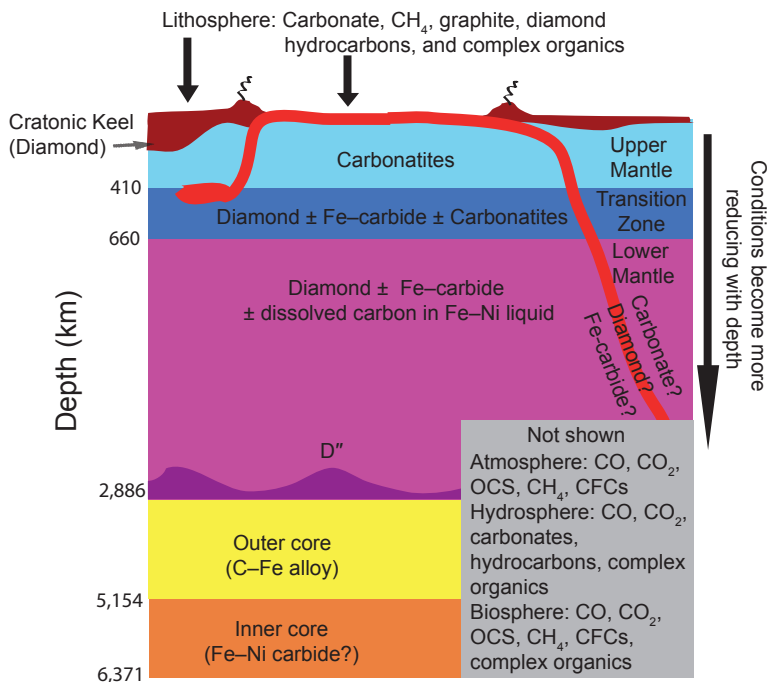


FIGURE 5 A summary of the known and hypothetical deep carbon reservoirs, but with no estimates of mass or relative proportions. Abbreviation: CFCs = chlorofluorocarbons

In addition, carbon isotope fractionation between metal-silicate systems preferentially sequesters the lighter isotope into the metallic phase(s) (Horita and Polyakov 2015). Therefore, isotope fractionation during carbon sequestration into the core would affect the carbon isotope composition of our planet, effectively increasing the ¹³C/¹²C ratio of the silicate portion of the planet (Mikhail et al. 2014). Thus, although the $\delta^{13}\text{C}$ value of the convecting upper mantle is statistically well constrained based on the study of mantle-derived samples, it is conceivable that the $\delta^{13}\text{C}$ value of the bulk Earth is different from that of the convecting upper mantle, or that the $\delta^{13}\text{C}$ value of the modern bulk Earth might not reflect the initial $\delta^{13}\text{C}$ value of the primitive Earth and/or its precursor bodies.

SUMMARY

Earth presumably accreted well within the snow line and the soot line, in a volatile-depleted region of the solar system. However, we know that Earth contains carbon, and that the H, C, and N isotopes point to a carbonaceous chondrite source for the terrestrial volatiles. Therefore, it is possible, and likely, that some of the material which formed the Earth originated from larger heliocentric distances. Because a significant fraction of early accreted carbon would have entered Earth's core during differentiation, the (isotopically) CI chondrite-like volatiles must have been delivered to the terrestrial planet-forming region after core formation. However, the timing and mechanism(s) of carbon delivery remain a matter of debate. We know that Earth accreted a significant fraction of its present-day mass during late accretion events, but the delivery of volatile elements (such as C, N, Ar) during the late veneer cannot dominate Earth's volatile budget. Earth is still accreting volatile-rich extraterrestrial matter today, with a flux of tens of thousands of kilograms per annum via micrometeorites.

The distribution of carbon in the different terrestrial reservoirs is not fixed, and the geological record is rife with externally and internally driven perturbations. For

example, Earth's surficial carbon reservoirs are perturbed by bolide impacts, some of which had dramatic environmental consequences (Kamber and Petrus 2019 this issue). We are also faced with one significant and inherent limitation: sampling Earth's interior is rife with sampling biases, restrictions, and the influence of surficial material emplaced into the mantle via subduction zone plate tectonics. In short, most geological samples originate from depths of less than 100 km (of Earth's 6,371 km radius) and only a few minerals (chiefly diamond) show tentative evidence for a deeper mantle origin. The most obvious limitation is that we will never obtain samples of Earth's core.

Owing to the uncertainties outlined in this article, we use caution and choose not to make bold and biased claims as to our opinion for the relative proportions of the celestial components which make up Earth's cosmic cocktail. The long-standing enigma of the origins of Earth's carbon is a dynamic problem, which is much larger in scope than planet Earth itself. The answers are undoubtedly going to rely on a collaborative approach requiring advances in experimental, analytical, and computational technologies between geochemists, geophysicists, planetary scientists, and cosmochemists. The least studied, but accessible, part of the puzzle focuses on the provenance and distribution of carbon throughout the solar system. For example, samples from primitive carbon-rich asteroids are going to be

returned to Earth in the early 2020s by two dedicated space missions: Hayabusa2, from Japan's JAXA, and OSIRIS-REx from USA's NASA. The milligram-sized samples, alongside data from cometary missions (Europe's ESA Rosetta Mission), will provide exceptional, essential, and priceless information on the nature of carbon in the early solar system. This will enable a more robust assessment of the formation and evolution of Earth's volatile reservoirs. To build upon the wealth of current and future terrestrial geoscientific datasets, we propose that such internationally collaborative planetary exploration missions, inclusive of sample-return objectives, are the best way forward to determine the relative proportions of the cosmic cocktail and to solve the mystery(s) of Earth's carbon.

ACKNOWLEDGMENTS

SM acknowledges support from the National Environmental Research Council (grant no. NE/PO12167/1) and the Carnegie Trust for the Universities of Scotland (grant no. RIG007794). EF acknowledges funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement no. 715028). This is CRPG-CNRS contribution 2720. We are grateful to Dr Conel M.O'D. Alexander and one anonymous reviewer for their constructive input, and the issue editors for their invitation to contribute. ■

REFERENCES

- Albarède F (2009) Volatile accretion history of the terrestrial planets and dynamic implications. *Nature* 461: 1227-1233
- Alexander CMO'D, Cody GD, De Gregorio BT, Nittler LR, Stroud RM (2017) The nature, origin and modification of insoluble organic matter in chondrites, the major source of Earth's C and N. *Geochemistry* 77: 227-256
- Bergin EA, Blake GA, Ciesla F, Hirschmann MM, Li J (2015) Tracing the ingredients for a habitable earth from interstellar space through planet formation. *Proceedings of the National Academy of Sciences of the United States of America* 112: 8965-8970
- Carlson RW, Borg LE, Gaffney AM, Boyet M (2014) Rb-Sr, Sm-Nd and Lu-Hf isotope systematics of the lunar Mg-suite: the age of the lunar crust and its relation to the time of Moon formation. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 372, doi: 10.1098/rsta.2013.0246
- Chou C-L (1978) Fractionation of siderophile elements in the Earth's upper mantle. *Proceedings of the 9th Lunar Planetary Science Conference*, 1: 219-230
- Dasgupta R, Buono A, Whelan G, Walker D (2009) High-pressure melting relations in Fe-C-S systems: implications for formation, evolution, and structure of metallic cores in planetary bodies. *Geochimica et Cosmochimica Acta* 73: 6678-6691
- Deines P (2002) The carbon isotope geochemistry of mantle xenoliths. *Earth-Science Reviews* 58: 247-278
- Fischer-Gödde M, Kleine T (2017) Ruthenium isotopic evidence for an inner solar system origin of the late veneer. *Nature* 541: 525-527
- Foley BJ (2015) The role of plate tectonic-climate coupling and exposed land area in the development of habitable climates on rocky planets. *Astrophysical Journal* 812, doi: 10.1088/0004-637X/812/1/36
- Füri E, Marty B (2015) Nitrogen isotope variations in the solar system. *Nature Geoscience* 8: 515-522
- Grady MM, Wright IP (2003) Elemental and isotopic abundances of carbon and nitrogen in meteorites. *Space Science Reviews* 106: 231-248
- Grewal DS, Dasgupta R, Sun C, Tsuno K, Costin G (2019) Delivery of carbon, nitrogen, and sulfur to the silicate Earth by a giant impact. *Science Advances* 5, doi: 10.1126/sciadv.aau3669
- Hauri EH and 6 coauthors (2017) Origin and evolution of water in the Moon's interior. *Annual Review of Earth and Planetary Sciences* 45: 89-111
- Hin RC and 9 coauthors. (2017) Magnesium isotope evidence that accretional vapour loss shapes planetary compositions. *Nature* 549: 511-515
- Horita J, Polyakov VB (2015) Carbon-bearing iron phases and the carbon isotope composition of the deep Earth. *Proceedings of the National Academy of Sciences of the United States of America* 112: 31-36.
- Kamber BS, Petrus JA (2019) The influence of large bolide impacts on Earth's carbon cycle. *Elements* 15: 313-318
- Kato C, Moynier F, Valdes MC, Dhaliwal JK, Day JMD (2015) Extensive volatile loss during formation and differentiation of the Moon. *Nature Communications* 6, doi: 10.1038/ncomms8617
- Kelemen PB, Manning CE (2015) Reevaluating carbon fluxes in subduction zones, what goes down, mostly goes up. *Proceedings of the National Academy of Sciences of the United States of America* 112: E3997-E4006
- Kress ME, Tielens AGGM, Frenklach M (2010) The 'soot line': destruction of polycyclic aromatic hydrocarbons in the terrestrial planet-forming region of disks. *Advances in Space Research* 46: 44-49
- Lodders K (2003) Solar system abundances and condensation temperatures of the elements. *Astrophysical Journal* 591: 1220-1247
- Lyons JR, Gharib-Nezhad E, Ayres TR (2018) A light carbon isotope composition for the Sun. *Nature Communications* 9, doi: 10.1038/s41467-018-03093-3
- Marty B and 8 coauthors (2016) Origins of volatile elements (H, C, N, noble gases) on Earth and Mars in light of recent results from the ROSETTA cometary mission. *Earth and Planetary Science Letters* 441: 91-102
- McDonough WF, Sun S-S (1995) The composition of the Earth. *Chemical Geology* 120: 223-253
- Mikhail S and 7 coauthors (2014) Empirical evidence for the fractionation of carbon isotopes between diamond and iron carbide from the Earth's mantle. *Geochemistry, Geophysics, Geosystems* 15: 855-866.
- Porcelli D, Pepin RO (2003) The origin of noble gases and major volatiles in the terrestrial planets. *Treatise on Geochemistry* 4: 319-347
- Raymond SN, Izidoro A (2017) Origin of water in the inner solar system: planetesimals scattered inward during Jupiter and Saturn's rapid gas accretion. *Icarus* 297: 134-148.
- Walsh KJ, Morbidelli A, Raymond SN, O'Brien DP, Mandell AM (2011) A low mass for Mars from Jupiter's early gas-driven migration. *Nature* 475: 206-209
- Wood BJ, Li J, Shahar A (2013) Carbon in the core: its influence on the properties of core and Mantle. *Reviews in Mineralogy and Geochemistry* 75: 231-250
- Woods PM, Willacy K (2009) Carbon isotope fractionation in protoplanetary disks. *Astrophysical Journal* 693: 1360-1378 ■