The value of CHONS isotopic measurements of major compounds as probes of planetary origin, evolution, and habitability

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1. Executive Summary

Carbon, hydrogen, oxygen, nitrogen, and sulfur (CHONS) are key ingredients for life, as well as components of volatile compounds that drive geological activity in many environments. CHONS isotopic ratios are a powerful tool for addressing critical questions in planetary science (Table 1). Existing isotopic measurements demonstrate the value of these data for understanding planetary origins and evolution and provide a roadmap for using isotopes to search for biosignatures. To address the science questions outlined in this white paper, we recommend investment in critical technologies (Table 4) that enable isotopic measurements of extraterrestrial materials with high sensitivity, precision, and accuracy, including: **(1) Sample preparation, separation, and introduction technologies for direct sampling and returned sample analyses; (2) Mitigation and reduction of contamination, including low-outgassing materials, maintaining spacecraft cleanliness through launch, and lessons learned from current and past missions; (3) Curatorial and calibration facilities; (4) Laboratory and modeling studies to develop frameworks for the interpretation of mission data.** These capabilities will support investigation of possible mission targets that include Mars sample return, Ocean Worlds, the ice giants, comets, Kuiper Belt Objects (KBOs), and inner solar system targets including the Moon, Mercury, and Venus.

Table 1. *Isotopic measurements have demonstrated value in addressing high priority science questions. Examples of potential future opportunities for scientific progress are highlighted.*

Theme	Relevant V&V Priority Science Questions	Past Isotopic Constraints	Future Opportunities (Traced to Table 4 Targets)
(1) Origins / Building new worlds	What were the initial stages, conditions, and processes of solar system formation and the nature of the interstellar matter that was incorporated?	- Relationship between meteorites, Earth, Moon, Mars via three-oxygen isotope map - Stellar origins of presolar grains via C, O and N isotopes	(1A) Origin of volatiles at the Moon, Mercury, asteroids, comets, Mars, and/or the outer solar system via CHONS isotopes, and especially HON
	How did the giant planets and their satellite systems accrete, and is there evidence that they migrated to new orbital positions?	- Origin of Titan's atmosphere via N isotopes - Origin and source materials for select Saturnian satellites via C and H isotopes - Hypothesis of different Jovian and Saturnian volatile reservoirs via D/H	(1B) Nature and origin of C, O, and N in giant planets, as well as noble gases (1C) Origin of water in Jovian satellites via H and O isotopes
	What governed the accretion, supply of water, chemistry, and internal differentiation of the inner planets and the evolution of their atmospheres, and what roles did bombardment by large projectiles play?	Relationship between water at Mars and Earth and small bodies via D/H measurements of comets and carbonaceous chondrites	(1D) Nature and origin of H and O at Venus via measurements of atmosphere and surface material for comparison to other inner planets (1E) Relationship between Main Belt Comets and inner solar system water via H and O isotopes
(2) Evolution/ Workings of solar systems	Can understanding the roles of physics, chemistry, geology, and dynamics in driving planetary atmospheres and climates lead to a better understanding of climate change on Earth?	Cycling of Martian materials between surface and atmosphere via CHONS isotopic measurements, including S in meteorites	(2A) Constrain atmosphere-surface interactions and volatile cycling at Mercury, Venus, Mars, Io, Titan, Triton, and Pluto via CHONS isotopic measurements for comparative planetology
	How have the myriad chemical and physical processes that shaped the solar system operated, interacted, and evolved over time?	Comparisons of isotopic ratios in different solar system materials and bodies to compare	
(3) Bio-signatures / Planetary habitats	What were the primordial sources of organic matter, and where does organic synthesis continue today?	Identification of low-temperature origins for chondritic organics via H and N isotopes; relationship between chondritic organics and carbonates via C isotopes	(3A) Isotopic measurements of organic material on Ceres, Europa, Titan, Enceladus, Triton, and Pluto and other Kuiper belt objects
	Did Mars or Venus host ancient aqueous environments conducive to early life, and is there evidence that life emerged?	Constraints on evolution of volatile reservoirs at Mars via H and O measurements of surface and atmosphere, and at Venus via H isotopic measurements of atmosphere	(3B) H and O isotopic measurements of Venus atmosphere and surface material (3C) CHONS isotopic measurements in organic material and sulfates/sulfides returned from Mars
	Beyond Earth, are there modern habitats elsewhere in the solar system with necessary conditions, organic matter, water, energy, and nutrients to sustain life, and do organisms live there now?	Terrestrial framework for H and C isotopic characteristics of biotic and abiotic compounds (including ongoing work)	(3D) Search for biosignatures on potentially habitable bodies, including: (3D1) Compound-specific isotopic analyses in organic material from Enceladus' plume (3D2) Isotopic ratios in bulk organic material and inorganic baselines (e.g., Ceres, Europa, Enceladus, Mars)

			• (3D3) Measurement of simple molecules with multiple rare ("clumped") isotopes

2. Introduction

Measurement of isotopic ratios is an essential tool for identifying the source and evolution of not only geologically and biologically important compounds but also planetary bodies. The mass difference in two isotopes of a given element (e.g., ^{13}C and ^{12}C) can lead to separation ("isotopic fractionation") between phases, among different compounds, through reaction networks, or via physical processes (Table 2). Measurement of the isotopic ratios of a given compound combined with geological context can therefore provide valuable insight into the compound origins and/or a record of physical, chemical, or biological processes [1].

Table 2. *The processes summarized here are important to planetary origins, planetary evolution, and biotic processes because they fractionate isotopes, creating measurable signatures.*

Type of fractionation	Relevant processes	Examples of applications/occurrence
Mass-dependent fractionation	Equilibrium fractionation	Geothermometer, especially for high temperatures
	Distillation processes	Cloud formation or melt crystallization
	Kinetic processes	Diffusion, evaporation, atmospheric loss to space, enzymatic mediation
Mass-independent fractionation	Photochemical processes	Relevant to planetary atmospheres and the protoplanetary disk

3. Origins

What were the initial stages, conditions, and processes of solar system formation and the nature of the interstellar matter that was incorporated? Isotopic ratios provide critical information about the early solar system. Application of oxygen isotope ratios to identify mixing of reservoirs as a significant process in the protoplanetary disk may be the most widely used example [2,3]. In addition, O, C and N isotopes in presolar grains have been used to identify the type of star from which the grains formed, and the high $^2\text{H}/^1\text{H}$ (D/H) and $^{15}\text{N}/^{14}\text{N}$ ratios of chondritic organics are commonly interpreted as evidence for formation at low temperatures. Further work is needed to understand the relationship between primitive isotopic reservoirs such as presolar grains, chondritic organics, and primordial water, and the current distribution of volatiles throughout the solar system. **Future measurements of CHONS isotopic ratios in volatiles from the inner and the outer solar system, including sample return from small body populations, are needed to advance understanding of the processes key to solar system formation.**

How did the giant planets and their satellite systems accrete, and is there evidence that they migrated to new orbital positions? In the Saturnian system, isotopes constrain conditions both in the subnebula and at the birthplace of Phoebe. Titan's nitrogen isotope ratio differs considerably from solar and predicted cometary N_2 ratios, but is similar to NH_3 ice in comets [4], consistent with Titan's accretion from materials processed in a warm Saturnian subnebula [5]. However, the D/H and $^{13}\text{C}/^{12}\text{C}$ ratios [6] measured at Phoebe suggest that it formed at greater heliocentric distances and/or out of the plane of the protoplanetary disk, where photochemical processing of CO_2 fractionated ^{13}C and ^{12}C [7]. **Additional insights into the origins of planetary systems are likely to arise from in-situ CHONS isotopic ratios of giant planet atmospheres, as well as their satellites' volatiles.**

What governed the accretion, supply of water, chemistry, and internal differentiation of the inner planets and the evolution of their atmospheres, and what roles did bombardment by large projectiles play? The Rosetta mission made isotopic measurements of volatile CHONS (as well as Xe, Ar, and Si) at Comet 67P/Churyumov-Gerasimenko [8]. Notably, the D/H ratio for Comet 67P is

$\sim 3\times$ higher than the terrestrial ratio, suggesting that the role of 67P-like comets in delivering water to Earth may have been small compared to carbonaceous chondrites [9]. However, more data are needed to constrain volatile delivery to the inner solar system as a whole, as well as to determine the primordial relationship between small body source reservoirs. Interpretation of the D/H ratio in the Venusian bulk atmosphere—the value of most significant interest for disentangling the history of water abundance and loss at Venus—is hampered in part by potentially conflicting data: Pioneer Venus D/H and Venus Express D/H differ by a factor of three, although the measurements were made below and above the clouds, respectively [10,11]. **High-precision D/H measurements throughout the Venusian atmosphere will enable discrimination among hypotheses regarding the volume, flux, timing, altitude-dependence, and processes affecting water (and, hence, the prospects for past habitability) on Venus. Complementary high-precision $^{18}\text{O}/^{16}\text{O}$ measurements of H_2O or refractory mineral phases [12] could provide additional constraints. Measurement of D/H and $^{18}\text{O}/^{16}\text{O}$ in hydrous phases at active asteroids in the main belt will clarify relationships between different small body reservoirs and the source of volatiles in the inner solar system [13].**

Figure 1. Trends in isotopic “maps” of solar system worlds, such as mixing of reservoirs (bottom left and top right corners of left panel), outliers (Phoebe in middle panel), and gradients (right panel) have helped unravel the origins of the solar system. More subtle trends reveal the imprint of evolutionary processes (e.g. atmospheric escape on Mars and Venus, right panel), including life. Many worlds and materials are still missing from these maps; so is the understanding that could stem from such measurements. Adapted from [7].

4. Evolution

Can understanding the roles of physics, chemistry, geology, and dynamics in driving planetary atmospheres and climates lead to a better understanding of climate change on Earth?

Comparative planetology provides context for interpretation of planetary climates. Martian isotopic data provide insight into atmospheric loss processes (Fig. 1 right panel). Enriched D/H and $^{15}\text{N}/^{14}\text{N}$ ratios in the Martian atmosphere confirm conclusions from $^{38}\text{Ar}/^{36}\text{Ar}$ data that a substantial fraction of Mars’ original atmosphere has been lost over time [14-17]. Sequestration as carbonate may also have significantly altered the abundance of atmospheric CO_2 and may even have exceeded escape to space during the Hesperian [18]. **Future measurement of $^{13}\text{C}/^{12}\text{C}$ in Martian carbonates as a function of age [19] would extend understanding of carbon sinks on hydrologically active bodies beyond Earth. Obtaining any isotopic knowledge on Venus surface materials would begin to constrain the evolution of its climate, providing a third data point for solid planets and insight into Earth’s possible far-future.**

How have the myriad chemical and physical processes that shaped the solar system operated, interacted, and evolved over time? Oxygen isotopic analyses of minerals in carbonaceous chondrites have provided strong constraints on their early aqueous alteration. Mass-dependent oxygen isotopic data have been used as a geothermometer [20], while mass-independent trends indicate mixing between the fluid and mineral phases, constraining open vs. closed system alteration [21,22] and time frame. **Comparable future isotopic measurements on other planetary bodies and returned samples can provide strong constraints on environmental parameters such as temperature, closed or open system behavior, mixing of different reservoirs [20-22], as well as photochemical processes responsible for mass-independent effects [23-25]. Relevant laboratory data are crucial for accurate interpretation of data acquired from extraterrestrial samples.**

5. Biotic Processes

On Earth, organisms fractionate isotopes of H, C, N, and S during uptake, cellular development, and metabolism. **Large fractionations are observed in H, C, N, and S isotope systems, suggesting that evidence for life could be identified in a planetary system from stable isotope measurements (Fig. 2).** Indeed, stable isotopes of carbon and sulfur are often used to support claims of the earliest life on Earth [26], using modern-day observations of biological isotope fractionation. Biological isotope fractionation can be observed in several forms: mineral/rock deposits, organic matter, and trapped or escaping gases.

Figure 2. $\delta^{13}\text{C}$ for typical inorganic (blue) relative to organic (green) sources demonstrates the characteristic large isotopic fractionation generated by biology. Figure adapted from [28].

It is imperative for astrobiology to understand isotope fractionations for chemosynthetic pathways in varied conditions (e.g., temperature, oxidation state) and how such records could change over time. For example, biotic and abiotic processes lead to different C but similar H fractionations in methane [27]. This provides a framework for evaluating methane C and H isotopes on Mars or Titan for possible biosignatures, provided such fractionations are understood in specific planetary conditions, such as the effects of Titan's atmospheric chemistry and escape.

The S isotope system is also often used to describe the modern and ancient influence of sulfate-reducing microbes in anaerobic systems. As seawater sulfate is consumed by modern organisms, the fraction of ^{34}S in unconsumed sulfate increases relative to ^{32}S [29] whereas H_2S produced by these microbes is depleted in ^{34}S to an extent controlled by microbial species, sulfate concentration, and rate of respiration [30-32]. Such fractionations have been recorded in sulfate minerals or sulfate bound in the crystal lattice of carbonate minerals, as observed in terrestrial rocks > 2 Ga [33,34], with low $\delta^{13}\text{C}$ in associated minerals suggesting a biological source [35]. Sulfate minerals are thus good targets for biosignature evaluation by in situ and sample return missions.

There are challenges in using isotopic biosignatures. First, all abiogenic mechanisms must be ruled out before an isotopic signature can be accepted as biogenic. For example, the Sample Analysis at Mars (SAM) mass spectrometer on the Mars Science Laboratory (MSL) has measured a range in $\delta^{34}\text{S}$ of sulfate and sulfide minerals comparable to that produced by

biological systems on Earth. However, equilibrium fractionation and photochemistry together provide a feasible abiotic source for these observations [36]. Second, the magnitude of metabolic fractionation is affected by the concentration of electron donors and acceptors, the metabolic and burial rates, and the overall biotic productivity. Third, terrestrial microbial ecosystems typically change with depth due to the type and availability of electron acceptors (e.g., O_2 or SO_4^{2-}). Zones of microbes may interact over variable spatial scales, producing complex mixing trends (e.g. Fig. 6 in [37]). Fourth, in situ analysis of organic and mineral samples typically requires significant sample processing. **Despite these challenges, biological isotopic trends appear to be predictable, and therefore are prime candidates for biosignatures. Thus, continued advancement of isotope analytical techniques for biosignature detection is crucial.**

6. Advances in Technology and Techniques

Direct, in situ sampling of planetary environments enables determination of variability in terms of time, space, or both via multiple measurements with moderate sensitivity and high precision. The most common methods include mass spectrometry (MS) and tunable laser spectroscopy (TLS). On Mars, isotopic compositions of atmospheric gases and gases evolved from heated samples have been measured by the SAM instrument suite, which combines MS and TLS, each focusing on different targets for highest precision. For Europa Clipper, the MAss Spectrometer for Planetary EXploration (MASPEX) has high sensitivity and high mass resolution to remove isobaric interferences [38]. In-situ millimeter wave spectroscopy has demonstrated very low mass and power resources, while enabling < 10 percent level isotopic measurements in a broad range of compounds [39].

Remote sensing via flight and ground-based spectroscopy enables acquisition of a large number of measurements (including surveys) for a wide variety of mission architectures. Submillimeter-wave spectroscopy is a mature technique for isotopic measurements in cometary comae: Rosetta/MIRO measured oxygen isotopologues of H_2O in the vicinity of 67P [40], Herschel/HIFI measured O and H isotopes at 103P from 0.2 AU [41], and SOFIA measured D/H at 46P [42]. The Atmospheric Chemistry Suite (ACS) FTIR has measured martian gases as part of the ExoMars mission [43]. At high enough column densities, the long pathlength enables determination of hard to observe ratios like $^{13}C/^{12}C$ and $^{18}O/^{16}O$ in CO_2 . Spatial Heterodyne Spectrometers (SHS) [44,45] allow both direct and remote isotopic measurements. SHS are ideally suited to measuring targeted spectral signals from angularly extended targets such as planetary gases, exospheres and plumes with a small bandpass range from far-UV [46,47] to IR wavelengths [48]. Several SHS-based instruments have flown on sounding rockets [46], and in low-Earth orbit [49,50]. Observations of Titan CO isotopes [51] and D/H of water in the Martian atmosphere [52] demonstrate the value of continued application of ground-based observatories to planetary targets.

Laboratory analyses of planetary materials offer high sensitivity and, in some instances, spatial resolution at sub-mm or better scales. Spatially resolved isotopic ratios can be obtained using Secondary Ion Mass Spectrometry (SIMS) or nanoSIMS, providing valuable petrologic context. Nuclear magnetic resonance (NMR) can be performed non-destructively, but has reduced sensitivity overall and does not provide petrologic context. Recent developments in laboratory analysis include position specific isotopic measurements, currently made via NMR [53] or pyrolysis-MS. For a molecule such as CH_3COOH , acetic acid, such measurements can distinguish the carbon isotope ratio for the CH_3 position from the $COOH$ position. Such data show strong promise, but further development is needed to establish rigorous context for

interpretation, as well as support more sensitive measurements via MS [54]. Other promising techniques include atomic probe tomography (APT), which can spatially resolve isotopic heterogeneity in nanoscale materials such as presolar grains [55].

Table 3. Summary of techniques used for isotopic analyses with current challenges and opportunities for investment in the next decade

Technique	Unique capabilities	Current challenges	Potential advancements	Impact of Investment
Mass spectrometry (direct sampling)	• Measurement of broad range of compounds, including ability to survey unknown compounds	• Trade-off between sensitivity and instrument-analyte interactions • Contamination • Sample prep	• Improved front end separation and purification techniques (e.g. single and multi-dimensional GC, open source) • Low-outgassing spacecraft materials	• High precision measurement of trace isotopologues, including unknown compounds; measurement of isotopes in liquid and/or solid phase compounds; overall decrease in uncertainty and error
Tunable laser spectroscopy (direct sampling)	• High precision stable isotope ratios in C, H, N, O, S with low resource envelope	• Form factor for electronics • Contamination • Sample prep	• Increase TRL to 6 for all-digital miniaturized electronics based on Zynq chip and for detector array.	• Reduced resource requirements for measurement of targeted compounds in situ
Spatial Heterodyne Spectrometer (direct sampling, remote)	• At-a-distance and near-field targets	• Relatively little flight heritage	• Maturation of TRL	• Enhanced ability for surveys of targeted compounds in extended sources
Submillimeter Spectroscopy (remote)	• Measurement of broad range of compounds; observes from thousands to millions of km depending on antenna size and column density	• High power requirements • Only a few species can be measured simultaneously with one receiver; multiple channels are needed	• Maturation of low-mass and power instruments, including antenna	• Reduced resource requirements for measurement of targeted compounds remotely
Millimeter Spectroscopy (in-situ)	• Measurement of broad range of CHONS compounds in tenuous environment; low mass – low power – low volume	• Recent technique, little flight heritage	• Maturation of TRL to 6 to enable infusion in space missions • Adjustments to bandwidth/range of operation	• Low resource, in situ measurements
UV Spectroscopy (remote)	• Remote observation, multi-use (ices, isotopes, surface reflectance)	• Sensitivity and precision are limited	• Maturation of fine gratings • Increases in sensitivity	• Medium precision remote measurements for targeted species
Earth-based IR, submm, & mm spectroscopy (ground-based)	• Extremely high spectral resolution (mm spectroscopy) • Flexible and/or rapid application to targets	• Sensitivity and spectral resolution in spectral windows masked by Earth's atmosphere • Sensitivity to restricted atmospheric altitude range prevents bulk atmospheric measurement	• James Webb Space Telescope • SOFIA • Continued application of Atacama Large Millimeter/submillimeter Array to planetary targets	• Improved ability to conduct statistically significant datasets and/or test for temporal/seasonal effects beyond the lifetime of a given mission
Laboratory analyses	• High precision (sub-permil) • Spatial context for some techniques • Simultaneous measurement of multiple isotopes on given sample • Archiving ability for future use	• Mass interferences • Contamination • Sample prep	• Improved mass separation, sample prep, baking procedures	• Measurement of trace isotopologues • Lower blanks, enabling measurement of rare compounds

7. Potential Mission Applications

Prioritization of isotope data for many different mission concepts supports the goals of the science community as a whole (Table 1). Notably, while major patterns and trends will emerge with data from multiple environments (Fig. 1), many of the science questions outlined here can be significantly constrained by a single mission platform.

Table 4. Possible mission concepts in the coming decade that would be enhanced by the inclusion of isotopic measurements. MS = mass spectrometer, TLS = tunable laser spectrometer.

Target	Science Focus for Isotopes Measurement (Tracing Table 1 Opportunities)	Modality	Possible instrumentation
Interplanetary dust	Origins (CHON isotopes) {1A, 1D, 1E}	Dust telescope (>10 km/s impact)	Dust spectrometer [56]
Mercury	Origins, evolution of volatiles in end-member chemical environments {1A, 2A}	Lander	MS (volatiles; [57]), Laser-MS, TLS [58]
Venus	Origins, interior evolution, atmospheric evolution (noble gases) {1D, 2A, 3B}	Direct sampling of atmosphere and/or surface	MS, TLS
Mars	Origins, atmosphere-surface interactions, habitability {1D, 2A, 3C, 3D2, 3D3}	Rover	MS, TLS
		Sample return	Earth-based MS
Ceres	Origin science on volatiles (esp. H, O, N), organics evolution (C, O, N) [59,60] {1A, 1D, 3A, 3D2}	Lander	MS, TLS
		Sample return	Earth-based MS
Main belt comets	Origin of volatiles in inner solar system (H,O, N, C) {1D} [13]	Fly-through, orbiter	MS
Europa	Origins, Habitability (e.g., H, O, C) Prebiotic/exobiology (e.g., C isotopes) {1A, 1B, 1C, 3A, 3D2}	Orbiter, lander	MS
Io	Volcanic processes & volatile cycling; history of volcanism {2A}	Plume fly-through	MS
		Flyby or orbiter	UV spectrometer, submm wave spectrometer
Saturn	Origin science on volatiles (H, O, N, noble gases, etc.) {1B}	Atmospheric probe, ring skimmer [61]	MS, GCMS, TLS
Enceladus	Prebiotic/exobiology (e.g., C isotopes) {3A, 3D1, 3D2, 3D3}	Plume and surface sampling [62,63]	Evolved gas analysis via MS or TLS [64]
Titan	Origins, atmosphere, evolution, prebiotic chemistry {1A, 2A, 3A}	Quadcopter, boat, submarine	GCMS
Ice Giants	Origin science on volatiles (He, Ne, Ar, Kr, Xe, their isotope ratios, and certain stable gas isotopes, in particular $^{13}\text{C}/^{12}\text{C}$ and D/H, possibly $^{15}\text{N}/^{14}\text{N}$ and $^{34}\text{S}/^{32}\text{S}$) {1B}	Atmospheric probe down to >10 bar	GCMS [65], TLS
Triton	Origin and evolution via atmosphere composition (e.g., $^{15}\text{N}/^{14}\text{N}$) or ionosphere {2A, 3A}	Atmosphere (remote, fly-through), ionosphere (fly-through) or lander	UV spectrometer, GCMS, plasma spectrometer
Pluto	Origin and evolution via atmosphere composition (e.g., $^{15}\text{N}/^{14}\text{N}$) {2A, 3A}	Orbiter	UV spectrometer, submm wave spectrometer
Comet	Solar system origins and evolution {1A, 3A}	Sample return (short-period) Remote (e.g., smallsat flyby) (short- and long- period)	Earth-based MS Submm wave spectrometer [66]

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