



The value of returning a sample of the Martian atmosphere

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The elemental and isotopic abundances of major species in the Martian atmosphere have been determined, but analyses often lack sufficient precision, and those of minor and trace species are frequently not well known. Many important questions about the evolution and current state of Mars require the kind of knowledge that can be gained from analysis of a returned sample of the Martian atmosphere. Key target species include the noble gases, nitrogen, and various species containing carbon, hydrogen, and oxygen, such as methane. More detailed analyses will no doubt provide measurements of other species that will allow insights of their own. These volatiles can constrain the origin of the Martian atmosphere, exchange of volatiles between the surface and interior, polar processes, and (in the case of methane) the possibility of extant biology on Mars.

Mars atmosphere | Mars sample return | Mars

With the possibility of returning samples of Mars to terrestrial laboratories becoming more realistic as the Perseverance rover caches samples in Jezero Crater, it is important to remember the value of returning one or more high-quality samples of the Martian atmosphere. The composition, both of species and of isotopes within species, is the result of outgassing of the Martian interior, loss to space, interaction with the surface, interaction with ice and water, and probably other mechanisms. One of the most significant factors is that the atmospheric composition is intimately tied to the yet-to-be-understood history of the variability of the climate of Mars, which in turn is tied to the question of whether Mars has ever been habitable or even inhabited.

As is the case for returning other types of samples from Mars, a returned sample has several intrinsic advantages over other techniques for studying the atmosphere. Unlike ground-based telescopic observations, there is no competing signal from the terrestrial atmosphere that the information (light, for telescopes) passes through. Unlike atmosphere contained within samples of meteorites, the time and location of the sampling is known, there is no complication from an implantation mechanism, there is no interaction with terrestrial processes, the journey from Mars to Earth is shorter and the irradiation and temperature histories well-known. Unlike studies by orbiters or rovers, the analyses will be done by state-of-the-art laboratory facilities, with the highest achievable precision of the day and unconstrained by instrument size, weight, or power limitations inherent to spacecraft operations. Most importantly, since a portion of the sample will be retained for posterity, the precision of the measurements will not even be constrained by the state of the art at the time of the first analysis. As analytical capabilities inevitably progress, it will be possible to identify important trace species, and to make ever

more precise measurements of amounts and isotopic compositions, at ever smaller amounts. Furthermore, identification of the most pertinent questions to be answered will not be constrained by the knowledge and hypotheses available at the time of sampling.

This contribution will focus on the scientific reasons for studying the composition of the Martian atmosphere and the Martian science it can inform. But there are other reasons why a sample of the atmosphere is necessary to take our understanding of Mars to the next level.

First, the atmosphere provides a boundary condition on the interaction between the surface and atmosphere at present. Second, measurement of the composition of the Martian atmosphere provides a baseline for analyzing the head-space gas collected with solid samples. Since many of the Perseverance samples have been collected with the analysis of volatiles in mind, and since many of these volatiles may react with the Martian atmosphere in the head-space, knowing the composition of the pure atmosphere will make it possible to better understand what has happened to the solid samples during the time between when a solid sample was collected and the collection tube sealed and the time when that tube is opened in a terrestrial laboratory (assuming, of course, that the head-space gas from each tube is collected individually upon opening). Finally, since the Martian and terrestrial atmospheres differ isotopically, knowledge of the isotopic composition of the Martian atmosphere provides a means of determining whether terrestrial contamination has occurred, once the head-space gas and sample volatiles are analyzed.

Various aspects of the return of an atmospheric sample from Mars have been discussed recently in refs. 1–4. However, the idea is hardly new. Most notably, a mission to skim through the atmosphere and collect a sample of atmosphere and dust to be returned was a finalist for the Mars Scout Program in 2002 but was not selected (5). Not surprisingly, the science objectives for the atmospheric sample were similar to those iterated here.

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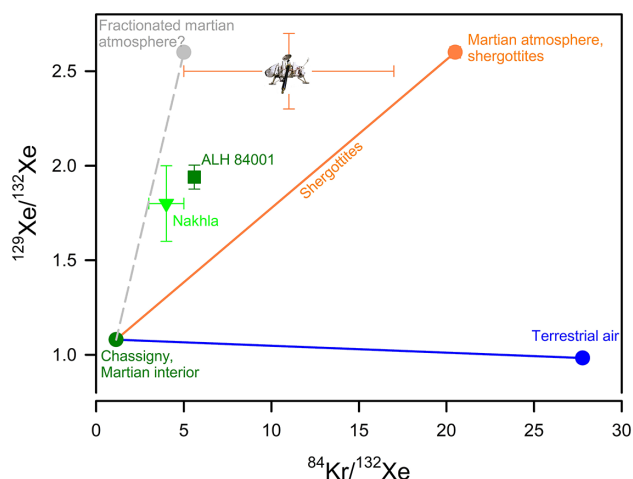


Fig. 1. Heavy noble gas isotopic and elemental compositions for selected Martian meteorites (see, e.g., refs. 26, 27, and 30). Note that the Viking lander measurement has uncertainties in the elemental Kr/Xe that essentially span the entire range observed within meteorites.

While we will frequently reference the current (as of mid-2024) plan to return samples collected by Perseverance, we will endeavor to address the value of a returned sample of the Martian atmosphere in a broader sense. In particular, we will consider some cases where the Perseverance samples would not be ideal. In some cases, a tube sealed by Perseverance would not contain enough gas for the necessary analytical precision, given the current state of the art (3); in others, such as the Kr/Xe elemental ratio discussed below, multiple samples, taken at different times, would be required. However, we believe that it is important to consider the full suite of measurements that might be used to answer important questions.

History of Knowledge of Martian Atmospheric Composition

Measurements of the composition of the Martian atmosphere have come from a patchwork of techniques, each with its own advantages and limitations. We highlight some of those here.

Before the age of spacecraft, the only information available was via spectroscopy from ground-based telescopes, which has the major limitation of having to separate spectroscopic lines due to the Martian atmosphere from those caused by Earth's atmosphere. One technique involved comparing the spectrum of Mars to that of the Moon—Kuiper (6) detected CO₂ in the Martian atmosphere this way. The other involved taking measurements when the planets' orbits meant that Mars had a significant Doppler shift—Spinrad et al. (7) detected water vapor in this fashion. Ironically, Percival Lowell and colleagues had sought to measure the amount of H₂O in the Martian atmosphere using both of these techniques (e.g., ref. 8), but with the instruments of the day, credible detections were not made. Decades later, though, the Doppler-shift technique was used for one of the early detections of Martian methane (9).

The mass spectrometer aboard the Viking lander measured the amounts of the trace species N₂, Ne, Ar, Kr, and Xe in situ at the surface of Mars and was able to determine that a few key isotopic ratios (¹⁵N/¹⁴N, ⁴⁰Ar/³⁶Ar, and ¹²⁹Xe/¹³²Xe) are very different from the terrestrial atmosphere. Although the

uncertainties on all the measurements were much larger than what can be done in a laboratory (sometimes by orders of magnitude), they were precise enough that when gases trapped in inclusions in basaltic meteorite EETA 79001 were measured and found to match the Viking measurements of the Martian atmosphere (and no other meteorites), that became the strongest early argument that EETA 79001 and related meteorites are Martian (10–12), a conclusion now widely accepted. This made it possible to make measurements of the noble gases, in particular, with the precision of laboratory mass spectrometers. However, corrections have to be made for interferences produced by cosmic-ray interactions during the rocks' long exposures in space, there is the possibility of interaction with the terrestrial atmosphere, and there is no knowledge of where on Mars the samples come from or when (time of day, season, or location in obliquity cycle) the atmosphere was implanted. Despite this, the isotopic measurements have been good enough to model the origin and evolution of the Martian atmosphere (13) and to determine questions that can be addressed with better measurements. With the knowledge that these meteorites are from Mars, isotopic ratios of other key elements, such as C, H, and O, in various minerals, can also be determined (e.g., refs. 14–18).

In many cases, the current state of the art when it comes to the composition of the Martian atmosphere comes from the Sample Analysis at Mars (SAM) instrument suite aboard the Curiosity rover. The presence of methane in the atmosphere, as well as its intermittent nature, have been confirmed (19, 20). The tunable laser spectrometer within the SAM suite made per-mil level measurements of the isotopic composition of CO₂ (21) and measured N isotopes to better than 10% (22). Finally, the isotopic compositions of Ar, Kr, and Xe, where the similarities between the Viking measurements and the meteorites were crucial in establishing the meteorites' Martian provenance, were measured (23, 24) with enough accuracy to basically confirm the meteorite measurements and to raise interesting questions in some areas. However, it was impossible to measure the isotopic composition of Ne or the elemental composition of the heavy noble gases Kr and Xe, leaving some key questions unanswered, as will be discussed below.

Examples of Specific Unanswered Questions 1: Noble Gases

The elemental and isotopic abundances of the stable noble gases (He, Ne, Ar, Kr, and Xe) reflect the balance between input to the atmosphere (production and/or outgassing of the planetary interior) and loss to space and record the history of these processes. The isotopic composition of the noble gases (other than He) has been studied for nearly 50 y, starting with the Viking lander measurements that clearly showed some of the differences between the terrestrial and Martian atmospheres (25). A considerable amount of effort has gone into studying the noble gases in Martian meteorites (e.g., see reviews in refs. 26–29). The SAM suite aboard Curiosity then measured the isotopic composition of Ar, Kr, and Xe at precisions comparable to the meteorite values (23, 24) and without the need for corrections for effects that occurred during the rocks' transits to Earth. While some questions remain for Ar, Kr, and Xe isotopes (for example, the

detailed explanation of what appear to be cosmic-ray-produced signatures in Kr and Xe), the most important questions remaining are in the atmospheric properties that Curiosity was unable to measure.

Kr/Xe Elemental Ratio. Shortly after the recognition that some meteorites are Martian, Ott (30) demonstrated that there appear to be at least three reservoirs of Kr and Xe in Martian meteorites. One, found in Chassigny, has long been interpreted as an interior reservoir. What was more puzzling is that he found two reservoirs that appear to have the same Xe isotopic composition, presumably that of the Martian atmosphere, but distinct elemental ratios of Kr to Xe (Fig. 1). Nearly 40 y later, the number of known Martian meteorites has increased from less than 10 to nearly 300, and many of these meteorites have been analyzed. Other Kr/Xe reservoirs have been found and, in some cases, explained, but the puzzle of the two “atmospheric” reservoirs has remained stubbornly mysterious. Typically, the “atmospheric” reservoir with the high Kr/Xe ratio is found in shergottite meteorites, and the one with the low Kr/Xe ratio in nakhlites, as well as the ancient meteorite ALH 84001. Many explanations have been suggested, but none has been accepted, at least in part because we do not know the Kr/Xe ratio in the current Martian atmosphere well enough.

The first meteorite in which the signature of the Martian atmosphere was found was EETA 79001 (10). The Kr/Xe ratio in the EETA 79001 gas is ~ 20 . This is the same (within uncertainties) as Viking’s measurement and is typically taken as the value for the Martian atmosphere (e.g., ref. 28). However, the Nakhla measurement by Ott (30) suggested a ratio of ~ 5 , which is also within the uncertainties of the Viking measurement but far different than the EETA 79001 value.

Which is actually the Martian atmosphere? Is there a process that fractionates Kr from Xe during incorporation into solids (e.g., ref. 31)? Or are they both actually the Martian atmosphere, but the ratio changes with time because Xe is sequestered by clathrates that form either seasonally or as the orbital obliquity changes (32–34) or by simply condensing or adsorbing? A crucial experiment would be to measure the Kr/Xe ratio in samples taken during different seasons—if there is a seasonal variation, it has important implications for the processes occurring in the polar regions. The Mars Sample Return mission as currently envisioned is unlikely to return more than a single dedicated atmospheric sample; there will be gases in the head-space of tubes containing rock samples and also in the witness tubes. Although the propensity of Xe to adsorb on surfaces will greatly complicate interpretation of these head-space gases, it is likely that in the course of analyzing the solid samples returned, it will be possible to determine how much Xe was originally in the head-space, for at least some of the samples. Or is there some other explanation altogether for the Kr/Xe variations? Without one or more atmospheric samples, the question will remain open, with intriguing possibilities unconstrained.

Ne Isotopic Composition. Mars loses atmospheric Ne to space on a timescale of 100 Ma or less, so the isotopic composition of neon is a balance between that loss to space and recent input, most likely from mantle degassing (34). Neon loss can be modeled relatively well, based on the observations of the MAVEN spacecraft (34, 35). Neon isotopes have been

measured in many Martian meteorites but are usually dominated by cosmic-ray-produced gas and are most commonly used to deduce cosmic-ray-exposure ages for the meteorites (e.g., ref. 36 and references therein). The meteorites with the largest atmospheric components present show clear signs of Martian atmospheric Ne, but estimates of the ratio of the two most abundant isotopes, $^{20}\text{Ne}/^{22}\text{Ne}$, range from ~ 7 to ~ 10 [(37) and references therein]. Martian meteorite Ne has been affected significantly by cosmic-ray production (hence its value for determining exposure ages) and, particularly in the case of desert meteorites, exchange with terrestrial reservoirs (38). A returned sample of Martian atmospheric Ne will cut through most of these complications and make more precise modeling possible.

He Elemental and Isotopic Composition. The lightest noble gas, He, has not been measured either in situ or in any atmospheric component in meteorites. Helium escapes readily from the terrestrial atmosphere, and escapes from the Martian atmosphere even more readily, and hence is rare. The only measurements of He in the Martian atmosphere are based on extreme ultraviolet spectra (39) and suggest an elemental abundance in the atmosphere of 10 ± 6 ppm. The ratio of the two isotopes, ^3He and ^4He , is completely unconstrained. As in the case of Ne, the abundance of each isotope of He represents a balance between input (presumably by mantle or crustal outgassing) and loss to space. Unlike Ne or ^3He , ^4He is being produced in copious quantities within the Martian interior by decay of U and Th. With a returned sample of the size of the Perseverance sample tubes, there should be enough ^4He (3) to make a sufficiently precise measurement of the abundance to make models with scientific relevance and to either make a relatively precise measurement of $^3\text{He}/^4\text{He}$ or at least set a scientifically useful upper limit on the ^3He abundance since the amount of ^3He is almost completely unconstrained at present.

Xe Isotopic Evolution. Before leaving the noble gases, it is worth commenting on one other noble gas topic that is potentially of great importance, but which will require more than just an atmospheric sample. Recent high-precision studies of rocks of various ages from Earth have shown that the Xe isotopic composition of Earth’s atmosphere has changed with time (40), with potentially profound implications for the history of atmospheric loss (41). The isotopic composition of Xe in the Martian atmosphere is consistent with a similar degree of loss (42), suggesting that an understanding of the history of Martian atmospheric Xe isotopic composition with time would have implications for both planets. However, even identifying the progression would require not only a high-precision measurement of a returned Martian atmospheric sample but also measurements of appropriate rock samples containing paleoatmosphere, which may not be possible until we have a much larger suite of returned samples than is currently envisioned.

Examples of Specific Unanswered Questions 2: Species Bearing C, H, N, and O

Like the noble gases, the abundance and isotopic composition of species involving the light elements C, H, N, O, and S are determined in part by the mechanisms of outgassing and

loss. However, these species are primarily of interest for the ongoing processes that they record.

Methane. The origin of methane gas on Mars is at the core of the question of whether there is extant microbial life there. The very presence of methane suggests an active source since it has a short atmospheric lifetime, on the order of 300 to 600 y, if only the photochemical lifetime is considered, but other processes might even shorten this (43). The variability observed similarly requires an active source. Whether that source is geological or biological, it implies some process operating at present that we do not yet understand.

Recent advances in using multiply substituted isotopologues of methane, $^{13}\text{CH}_3\text{D}$ and $^{12}\text{CH}_2\text{D}_2$ (18 amu), relative to the singly substituted isotopologues, have demonstrated that the mass-18 isotopologues are powerful tracers of the formation pathways of these gases. For example, a significant deficit in both $^{13}\text{CH}_3\text{D}$ and $^{12}\text{CH}_2\text{D}_2$ relative to expectations from a random distribution of isotopes across all CH_4 isotopologues is a tell-tale signature of microbial methanogenesis (44, 45), as is a distribution of isotopologues in thermodynamic equilibrium at low temperatures of $\sim 20^\circ\text{C}$. Similarly, abundances of these species in thermodynamic equilibrium at modest geological temperatures of ~ 100 to 200°C are a signature of thermogenic methanogenesis, and serpentinization is indicated as a source where thermodynamic equilibrium is established at higher temperatures of $\sim 300^\circ\text{C}$ (46). Oxidation of methane also has distinctive mass-18 isotopologue signatures. Some ambiguities remain, but in general, if the abundances of these rare isotopologues can be measured, a probability can be assigned to the origin of methane gases on this basis.

Methane is a trace species, with an abundance at the ppb level (by volume), low enough, in fact, that the amount of methane in a single tube collected by Perseverance does not contain enough methane for an isotopic analysis, given present technology (3). Nonetheless, analytical techniques continually improve, and even if the amount of methane in a sample (whether Perseverance tubes or something else) is not measurable at the time of the return, it likely will be in the not-too-distant future, as techniques evolve. For example, orbital ion trap Fourier-transform mass spectrometers are developing rapidly (47, 48) and should evolve to the point where rare isotopologues of methane can be measured in orders of magnitude less gas than at present. In fact, return of a Martian atmospheric sample might spur the improvement of methane analyses since the methane is a potential biosignature (although lack of biogenic methane does not rule out the possibility of microbial life on Mars).

N Isotopologues. Nitrogen in the Martian atmosphere is enriched in ^{15}N relative to gases released from shergottite meteorites (26, 49). Mixing trends between what appears to be high-temperature nitrogen in meteorites, with $\delta^{15}\text{N}$ values near zero relative to terrestrial air, and the Martian atmosphere, with $\delta^{15}\text{N}$ values of ~ 600 per mil, suggest that some fraction of an atmosphere nitrogen component is contained within the shergottite meteorites. An understanding of the exchange of nitrogen between rock and atmosphere on Mars would benefit from a tracer of the origin of N_2 based on $\delta^{15}\text{N}$ (i.e., $^{15}\text{N}/^{14}\text{N}$) alone.

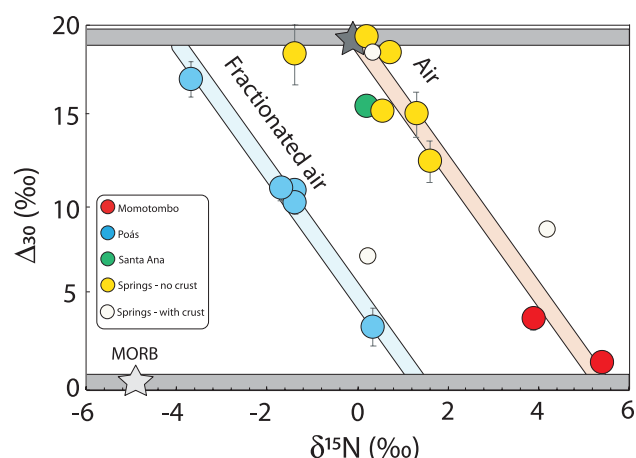


Fig. 2. Nitrogen isotopes in volcanic rocks from Central America (55). The gray bars at the top and bottom represent 100% air contamination and no air contamination, respectively. Note that a $\delta^{15}\text{N}$ of 0 could represent either 100% air contamination or near-zero air contamination; the ambiguity is resolved by measurement of $\Delta^{30}\text{N}$. Reprinted from ref. 55 with permission from Elsevier.

On Earth, it has been discovered recently that there is an excess of $^{15}\text{N}/^{14}\text{N}$ in air of 19.2 per mil (50). This new tracer for air, expressed as $\Delta_{30} = 19.2$ (the per mil excess in $^{15}\text{N}/^{14}\text{N}$ above that expected from a stochastic distribution of ^{15}N and ^{14}N atoms across all N_2 molecules), is now being used in terrestrial settings to deconvolve the effects of $^{15}\text{N}/^{14}\text{N}$ isotope fractionation of atmosphere from mixing between volcanic-derived dinitrogen and atmosphere (e.g., Fig. 2). This work is based on the observation that high-temperature nitrogen, and nitrogen produced by biological processes, has Δ_{30} values near zero per mil, compared with the atmosphere Δ_{30} value of 19 per mil. By correlating Δ_{30} values with other gas isotope ratios, including $^{40}\text{Ar}/^{36}\text{Ar}$, for example, these studies, e.g., ref. 51, have shown that Δ_{30} values can be used to remove, mathematically, the effects of atmosphere contamination in samples of putative high-temperature gases (e.g., volcanic hydrothermal gases). The positive Δ_{30} effect comes from reactions between ionized N and O in the upper atmosphere. A similar chemistry occurs in the Martian atmosphere (52), so there is a distinct possibility that the Martian atmosphere also has a characteristic and distinct Δ_{30} value. One expects that impact-implanted N_2 in glasses, for example, will retain this atmospheric signature. Once Δ_{30} is measured for a sample of pure Martian atmosphere, the degree to which $\delta^{15}\text{N}$ values in trapped gases are attributable to atmosphere as opposed to fractionation mechanisms can be deduced; endmember high-T isotope ratios, free of atmospheric contamination, can be obtained using Δ_{30} values as a tracer of contamination. Knowing the uncontaminated, igneous $\delta^{15}\text{N}$ for Mars helps to constrain its primitive building materials. Was it built from E-chondrite planetesimals, for example, with characteristic $\delta^{15}\text{N}$ values of between about -40 and 0 per mil (53, 54), or not?

Carbon Isotope Composition of Martian Atmospheric CO_2 and Carbonates. Data on the isotopic composition of carbon in the Martian atmosphere from Curiosity and Martian meteorites are similar (21, 56, 57), but distinct from the measurement by the Phoenix lander (58). Information about the composition of the Mars atmosphere could come from

carbonate minerals: Atmospheric CO₂ dissolves in water and increases the acidity, which leads to dissolution of Fe-bearing silicates, and eventually to precipitation of mainly Fe- and Mg-rich carbonates (59). The carbon isotope composition of CO₂ in the Mars atmosphere thus may also be reflected in the $\delta^{13}\text{C}$ of near-surface carbonates. Also, biological formation of carbonates (e.g., ref. 60 for ALHA84001) would leave behind a distinct isotope signature. A compilation of literature data (58) on Martian carbonates shows a range between –20 and 65 per mil, i.e., covering the entire range of data reported on the Mars atmosphere and Mars mantle. The carbonates hence only provide ambiguous information about the atmospheric composition. The reported $\delta^{13}\text{C}$ data for the Mars atmosphere along with the carbonate data clearly illustrate that measurements of the Mars atmosphere using modern laboratory techniques are required. Analyzing the carbon isotope composition of the atmosphere with high analytic resolution on samples that were sealed at different times during the Mars seasons would further provide information on the global carbon cycling on Mars.

Oxygen Isotope Composition of Atmospheric CO₂ and Carbonates.

Stable oxygen isotopes of CO₂ and carbonates are important tools for the understanding of evolution of the atmo- and hydrosphere. The $\Delta^{17}\text{O}$ of atmospheric CO₂ is of particular interest. Small deviations from a mass-dependent correlation between $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ are expressed in the form of the $\Delta^{17}\text{O}$ notation:

$$\Delta^{17}\text{O} = \ln(\delta^{17}\text{O} + 1) - 0.528 \times \ln(\delta^{18}\text{O} + 1). \quad [1]$$

Deviations on $\Delta^{17}\text{O}$ from zero can be due to mass-independent or mass-dependent fractionation processes. Photochemical reactions in the Mars atmosphere can lead to a modification of the $\Delta^{17}\text{O}$ through mass-independent effects (15, 61). Also, interaction with exchangeable Martian surface and near-surface water will influence the oxygen isotopes in atmospheric CO₂. Additionally, the release of juvenile CO₂ through igneous outgassing would release CO₂ with $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ close to that of bulk Mars.

A hint toward the $\Delta^{17}\text{O}$ composition of atmospheric CO₂ can be obtained from water and carbonates in Martian rocks. Water extracted at high temperatures from SNC meteorites Nakhla, Chassigny, and Lafayette (16) showed clear evidence for disequilibrium between the water and the rocks. The authors have discussed this observation in terms of preservation of a primordial isotope heterogeneity of volatile-rich (hydrosphere) and volatile-poor (lithosphere) reservoirs, photochemical reactions with mass-independent effects in the Mars atmosphere, or addition of volatiles by influx, e.g., of cometary material. Atmospheric CO₂ that had exchanged with such a water reservoir should have $\Delta^{17}\text{O}$ higher than bulk Mars. Apart from water extracted at high temperatures from rocks, carbonates also carry a positive ^{17}O isotope anomaly (15). Just like juvenile CO₂, juvenile water that outgassed from the mantle at high temperatures should not carry a positive $\Delta^{17}\text{O}$ relative to bulk Mars.

Where did the positive $\Delta^{17}\text{O}$ in water and carbonates come from? Photolysis (61), irreversible desublimation of vapor during winter and sublimation of ice during the summer season (62), and loss of CO₂ to space have all been

suggested (63). High-precision data on atmospheric CO₂ are key to untangling the issue. No usable $\Delta^{17}\text{O}$ data are available from Mars atmospheric CO₂. The variations related to the discussed processes are generally small (<1‰) and require laboratory-based measurements. Returned samples will resolve the questions about the composition of atmospheric CO₂ and the origin of the $\Delta^{17}\text{O}$ isotope anomalies observed in Martian rocks. In some cases, further improvements in analytical techniques (e.g., ref. 64) or instrumentation (e.g., ref. 65) may be required, but a returned sample is not subject to the state-of-the-art at the time of its collection.

Clumped Isotopes of Mars Atmospheric CO₂. The clumped isotope for CO₂, denoted by Δ_{47} , is the excess of $^{13}\text{C}^{16}\text{O}^{18}\text{O}$ (“clumped isotope”) over a random distribution of isotopes in a molecule and can be used (along with $\Delta^{17}\text{O}$ and $\delta^{13}\text{C}$) to trace the origin of atmospheric CO₂ (e.g., refs. 66, and 67). The enrichment in mass-47 (Δ_{47}) isotopologues is a function of temperature — Δ_{47} increases with decreasing temperature. Clumped isotope measurements have not been done on Martian atmospheric CO₂ but could provide insights into the exchange temperature between atmospheric CO₂ and the hydro- and cryosphere. Variations in Δ_{47} are small, and high precision is required. Currently, this can only be achieved by laboratory measurements.

Hydrogen in Martian Vapor and Rocks. The hydrogen isotope composition of the Mars mantle is suggested to be similar to that of Earth (17, 18). Martian atmosphere vapor, however, is enriched in deuterium by a factor of five, i.e., vapor has a $\delta\text{D} \approx 4,000$ per mil, however with a wide range from 1,000 $\leq \delta\text{D} \leq 9,000$ per mil (68). The large variations are due to seasonal effects, sublimation of ice during summer, and desublimation of vapor during winter. The enrichment is the result of the loss of approximately 80 to 95% of the surface water that existed on Mars.

The atmospheric vapor is only a subordinate water reservoir on Mars, amounting to only ~0.4 ppm of surface water (ice, adsorbed water). Most of the surface water is bound in the ice caps, subsurface ice, and adsorbed water on mineral surfaces. Due to the exchange between atmospheric water and the major surface reservoirs (e.g., seasonal sublimation, desublimation), the δD of the atmosphere (17) provides information on the current Mars hydrosphere. The Martian meteorites and their components hence span the entire δD range between juvenile Martian water ($\delta\text{D} \approx$ zero per mil) and highly δD enriched atmospheric vapor [$\delta\text{D} \approx 7,000$ per mil, modern Mars atmosphere (68). In situ measurements of water extracted from a ~3 Ga old mudstone by the SAM instrument on the Curiosity rover yielded $\delta\text{D} \approx 2,000$ per mil, i.e., three times the terrestrial value (69) and confirm high δD in Martian minerals and early loss of water from Mars. These exemplary data show that the enrichment in deuterium in atmospheric vapor is well established and understood in terms of the loss of water from Mars.

The measurement of δD on atmospheric vapor samples will be challenging due to the low water content and, in the case of rock sample headspace analyses, the possibility of exchange between the atmosphere and the rocks after sealing of the sample tubes. Dedicated atmospheric sample tubes would be crucial for obtaining data on the δD of Mars vapor.

Again, sampling at different times during the Mars season would be valuable in better understanding the diurnal cycling of vapor on Mars. The latter, in turn, would be important for better understanding the effect of diurnal cycling of water on the $\Delta^{17}\text{O}$ of CO_2 .

The Potential for Later Analyses Enabled by Returned Samples.

In the Introduction, we mentioned that one of the benefits of returned samples is the ability to analyze a sample using more advanced technology years, and even decades, later. In this section, we note one classic example of a prominent set of analyses of volatiles (albeit not atmosphere) decades after sample return, using technology that did not exist at the time of sample return, and then enumerate several places where a Martian atmospheric sample may become more useful in the not-too-distant future as techniques advance. When the Apollo lunar samples were returned from the Moon, attempted analyses of water contents concluded that the Moon was dry. Or at least, the amount of water that could be measured was no more than could be explained by the samples' interactions with the Earth (70, 71). However, as techniques improved, water was detected *within* grains using SIMS, secondary ionization mass spectrometry (72). In subsequent years, knowledge of the amount of water within specific grains in Apollo samples has been measured well enough to provide a mechanism for modeling water content of the lunar mantle [(73) and references therein].

Some specific cases where analytical improvement is needed have been cited above, but there are two more obvious ways that future analytical advancements could make a returned Martian atmospheric sample even more valuable.

One is the measurement of C and H isotopes within methane. Although the amount of atmosphere that could be returned within a Perseverance sample tube would not contain enough methane for a high-quality measurement, measurement techniques continue to improve, particularly for tunable laser spectrometers.

The other is the detection of species that may be below detection limits at the time of sample return. For example, we have not discussed any sulfur-bearing species because none are currently expected to be close to detection limits, but those detection limits will continually improve. Knowing what S-bearing species are present in what relative abundances will likely solve some problems, and introduce others, but the field is constrained only by upper limits at the moment.

Finally, knowing the composition of the current Martian atmosphere will make it possible to determine whether volatiles trapped within rocks, whether Martian meteorites or

returned Martian rocks, represent exchange with the current atmosphere. If not, these volatiles, whether in fluid inclusions or incorporated some other way, may be providing insights into the Martian paleoatmosphere.

Summary

A return of a sample of the Martian atmosphere would be able to answer several key questions:

- There appear to be two distinct atmospheric ratios of Kr to Xe in Martian meteorites. An atmospheric sample would, at the least, provide a critical constraint to begin to decide between models that have significant implications for the history of Martian climate.
- Measurement of the isotopes of Ne and He and even the abundance of He would make it possible to model the history of the competition between mantle outgassing and loss to space far more accurately.
- Measurement of the isotopologues of N would provide a critical constraint on processes going on within the current atmosphere of Mars.
- Measurement of the isotopes of C, H, and O in species like CO_2 and H_2O would provide information about processes including outgassing and isotopic fractionation during loss.
- Measurements of the isotopes of C and H in methane, though difficult at the time of return for the amounts in the tubes collected by Perseverance, are likely to become possible as technology develops and will provide critical input into the question of the origin of the variability of methane, including the question of whether it is geological or biological in nature.
- Other trace species are likely to be detected as time progresses, providing constraints and questions of their own, on topics like volcanic outgassing and the evolution of Mars as a geologically active planet.
- Taken together, understanding the Martian atmosphere fully is a key aspect of deciphering the likelihood that life has ever been active on Mars—and whether it still could be thriving in protected environments.

Data, Materials, and Software Availability. There are no data underlying this work.

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