Constraining the history of water and climate on Mars through light element stable isotope analysis of volatiles in returned martian samples

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Much has been learned about Mars through data returned from space missions and analyses of martian meteorites. There are, however, many questions still outstanding which cannot currently be answered—including the issue of whether there is, or was, life on Mars. The return of a cache of samples—including of the atmosphere—from separate locations in Jezero Crater and with differing petrogeneses will provide the international community with the opportunity to explore part of the evolutionary history of Mars in great detail. Specifically, measurements of the isotopic compositions of the light elements H, C, N, O, Cl, and S can be used to follow how volatile species cycle through the different martian volatile reservoirs (atmosphere, lithosphere, cryosphere, and hydrosphere). Measurement of isotopic fractionation enables inference of the environmental conditions (e.g., temperature, water/rock ratio) under which fractionation occurred. Knowing the contextual relationship of the materials to their geological settings, coupled with precise compositional measurements will enable a more thorough understanding of martian volatile history and allow a picture to be constructed of water and climate on Mars as represented at Jezero Crater.

volatiles | climate | water | carbon | isotopes

The first high-resolution images of the surface of Mars were obtained by NASA's *Viking 1* and *Viking 2* orbiting spacecraft. The images showed that the planet's surface was covered in a rich variety of features that indicated an extended and complex evolutionary history (1). Networks of valleys and channels were identified as potential dried-up river-beds (2), and a series of enormous mountains were believed to be ancient volcanoes (3). It was clear that Mars had experienced significant magmatic and fluvial activity throughout its past, leading to an understanding that volatiles must have played a key role in its evolution (4–6). Over the following five decades, continued exploration of Mars has allowed construction of comprehensive models for the origin and history of different volatile species, and how they interact with and transfer between different volatile reservoirs (7, 8). It is important to constrain the abundances and hosts of various volatile species—and how these may have changed with time—because that enables a view of how Mars' climate has changed and how this has affected the potential habitability of the planet (9). However, despite the plethora of images and physical and chemical data that have been collected by instrumentation on orbiting, landed, and roving spacecraft, complemented by comprehensive analyses of martian meteorites, there are still many unsolved questions about the evolution and habitability of Mars (10). It is recognized that the return of a suite of samples from Mars is required to resolve some of the outstanding issues, including the origin, distribution, abundance, and interactions of volatile species in different martian reservoirs (11). The Mars Sample Return campaign is at its first stage: rocks with both primary and secondary mineral phases that contain volatiles have been collected from the Noachian-aged Jezero Crater by the Perseverance rover (12–14). Primary minerals are those which crystallized directly from magma (e.g., olivine, pyroxene) and are a record of the initial materials from which Mars aggregated—such as the oxygen isotopic composition of the lithosphere, or the hydrogen isotopic composition of dissolved magmatic water. Secondary phases are minerals produced by alteration of the primary grains (e.g., phyllosilicates) or precipitation from fluids (e.g., carbonates, sulfates). They are records of later processes—e.g., the isotopic composition of water or CO_2 in contact with Mars' atmosphere. Comparison between the isotopic compositions of primary and secondary minerals (e.g., oxygen in magmatic olivine compared with the oxygen in phyllosilicates produced from alteration of olivine) should enable a better understanding of the martian volatile cycles, the interactions between atmosphere and lithosphere and how they are affected by changes in martian climate.

Significance

Mars has long been considered a planet with a high potential to have been habitable in the past, when it possessed a thicker atmosphere and water flowed over its surface. The paper describes how study of the volatile inventory of Mars will help comprehend when and how the atmosphere and hydrosphere disappeared and Mars became (apparently) uninhabitable. The Mars Sample Return Program is a crucial step in enabling the high precision analyses of a variety of rock and gas samples that are necessary to understand the interlocking volatile cycles of Mars.

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Mars Sample Return (MSR) has been a goal of the international community for several decades. Although one of the main drivers has been the search for life (extant or extinct) on Mars, the requirement for sample return also has many other scientific and technical objectives. A report (10) produced by the International Mars Sample Return Objectives and Samples Team (iMOST; a Committee established jointly by NASA and ESA) defined seven objectives specifically related to the science that could come from returned samples. Objective 4 (with 4 subobjectives) was expressly concerned with analysis of volatile species (Table 1). Here, I consider why analyses of returned samples are essential to understanding the volatile history of Mars, setting the discussion in the context of iMOST Objective 4 (10).

Determination of the abundance, speciation, and isotopic composition of volatiles in samples returned from Mars will aid in answering key questions about Mars' evolutionary history and its potential for harboring life. The elements and their isotopes discussed herein are hydrogen (D/H), carbon ($^{13}C/^{12}C$), nitrogen ($^{15}N/^{14}N$), oxygen ($^{16}O/^{17}O/^{18}O$), chlorine ($^{37}Cl/^{35}Cl$), and sulfur ($^{32}S/^{33}S/^{34}S/^{36}S$). Analysis of these isotopes will be undertaken on silicate minerals (including olivine, pyroxene, plagioclase, and phyllosilicates) and nonsilicates (including carbonates, nitrates, sulfates, sulfides, perchlorates, chlorides, and phosphates), as well as water, organic compounds, and atmospheric gases. Analysis of organic compounds and atmospheric noble gases are considered in companion papers (15, 16). Isotopic composition is reported in the delta (δ) notation as a parts per thousand (per mil; ‰) deviation in the ratio of minor to major isotope from the same ratio in an international standard. For example, for carbon:

$$\delta^{13}C = \frac{S - R}{R} \times 1000\%,$$

where S is the $^{13}C/^{12}C$ ratio of the sample and R is $^{13}C/^{12}C$ in the international standard. The standard for hydrogen and oxygen is Standard Mean Ocean Water (SMOW), for chlorine it is also seawater, Standard Mean Ocean Chloride (SMOC), for carbon, a fossil belemnite from the Pee Dee formation of South Caroline (PDB), for nitrogen is AIR and for sulfur, troilite (iron sulfide) from the Canyon Diablo meteorite (CDT).

Table 1. Objective 4 of the iMOST report, and its subobjectives (10)

Objective 4: Constrain the inventory of martian volatiles as a function of geologic time and determine the ways in which these volatiles have interacted with Mars as a geologic system

	Subobjective
4A	Determine the original source(s) of the planet's volatiles, and the initial isotopic compositions of the constituent gases in the atmosphere.
4B	Understand crustal–atmospheric interactions and feedbacks, especially for C, O, S, N, Cl, and H, in order to interpret present and past geochemical cycling on Mars.
4C	Quantify the history of the composition of the atmosphere, and the history of contributions from the interior (e.g., H, C, Cl, N, O, noble gases, and radiogenic products).
4D	Assess temporal (seasonal) variations in the composition of the present-day atmosphere to determine seasonal changes to both major and minor species as a means for evaluating crust-atmosphere cycling.

The isotopic compositions of volatile elements are diagnostic of their source reservoirs; they are modified by mixing and exchange between reservoirs and the physical processes that the reservoirs experience, such as heating (leading to evaporation or sublimation), cooling (leading to condensation), and diffusion. They can also be modified during chemical reactions. These processes are generally *mass-dependent*, i.e., the lighter isotope is fractionated from the heavier isotope during kinetic or equilibrium processes in a fashion that is proportional to the difference in masses of the isotopes. *Mass-independent* fractionation results from processes such as photolysis—the severing of bonds between atoms in a molecule by photons. There is an additional category of isotope fractionation where fractionation is mass-dependent, but not directly proportional to mass difference. This so-called "noncanonical" mass-dependent fractionation (17) is observed in processes such as breakdown of carbonates (18) and sulfates (19) by heating. Components resulting from the products of any of these fractionation mechanisms may retain a characteristic isotopic signature of the mechanism, which should assist in interpretation of how they formed.

Measurement of the isotopic composition of volatile species is a recurring theme throughout the iMOST report and is a focus of Objective 4 (Table 1). Four Investigation Strategies and 19 sets of discrete measurements were recognized as essential to address Objective 4 (10); to do so requires high precision and high spatial resolution analysis of material to ensure that the alteration history of a sample can be tracked and that any secondary effects from, e.g., isotopic exchange with other volatile sources subsequent to formation, are taken into account. For example, measurement of the isotopic composition of volatiles in primary (nominally anhydrous) minerals from unaltered Noachian-age basalts, such as those collected by Perseverance from the floor of Jezero Crater (13), will constrain the isotopic composition of the original volatiles preserved at the crater since Mars' formation. By analyzing volatiles in secondary minerals, formed by fluid alteration of the primary species, we should be able to follow how the volatiles have become distributed through different reservoirs (atmosphere-surface-interior) and see how volatile compositions have evolved. To track volatile species through the separate reservoirs requires a variety of materials, ranging from unaltered Noachian-aged igneous rock to samples of the contemporary atmosphere. This should help us to reconstruct the history of the processes that have shaped the materials collected at Jezero Crater and hence enable inferences about changes in Mars' climate. Although such signatures are measurable, they are often quite subtle and require high precision analysis, at levels achievable in a specialist laboratory, but not yet in space flight instrumentation. Hence the requirement for return of samples.

Volatile Cycles on Mars Compared with Earth

Like that of the Earth, the original source of Mars' volatiles was the protoplanetary disk and consisted of a diverse mix of starting materials, including ice and other volatiles from the outermost part of the solar nebula. Since most models for formation of the terrestrial planets have Earth and Mars forming "relatively" close to each other, the two planets were likely to aggregate from an approximately similar compositional mix of solids and gases (20, 21). However, as they cooled, the evolutionary histories of the two planets diverged and from ~20 My after aggregation the abundances (and isotopic compositions) of their constituents also followed different evolutionary tracks (22).

The terrestrial volatile cycle, or more accurately, series of cycles, is a complex interaction between atmosphere, hydrosphere,

cryosphere, lithosphere, and biosphere (23). This has led to the operation of both nonbiological and biological cycles. In the former, volatiles (in various species) are transferred between reservoirs through a series of processes, including dissolution of atmospheric species in surface and subsurface fluids, sedimentary rock formation, weathering of rocks, subduction at active plate boundaries and magmatic degassing back into the atmosphere. The biological cycle intersects with the abiological cycle during sedimentary rock formation. The system is not closed: volatiles are added to the Earth by meteorites and micrometeorites. The cycles are driven by plate tectonics and, in the most recent Era (the Anthropocene), have been moderated by anthropogenic input. Evidence for changing climate through time is clear in the stratigraphic record where differences in rock type can be keyed to geochemical signatures of temperature and $f(O_2)$ as well as sea-level (24).

Mars does not have an active tectonic plate system (25)—although some parts of the ancient surface hint that limited crustal cycling might have occurred (26). Results from the Insight lander have indicated that Mars' molten core is probably overlain by a layer of molten rock, acting as a heat source that delayed cooling of the lowest part of the mantle (27, 28). However, transfer of heat by convection from this boundary layer, upward into the upper mantle and crust would be limited (29) and thus have a reduced effect on cycling of volatiles between the lithosphere and atmosphere. So it is likely that the current cycling of volatiles on Mars would be different—and probably less complex—than that of Earth.

At present, there are two major reservoirs of martian volatiles: the martian atmosphere (currently mainly CO_2, with lesser amounts of nitrogen, noble gases, sulfur, and chlorine species) and the martian cryosphere: Mars' polar caps are mainly water ice, with varying abundances of CO_2 ice, depending on season. There is a subsurface permafrost layer, which at shallow depths (of the order of cm-scale) is pure water ice (30). The lithosphere is an important sink for volatiles; in the past, there was an extensive hydrosphere, but, so far, no direct evidence for a biosphere. The

lack of a hydrosphere and only a limited internal heat source implies that any abiological volatile cycle must now be almost static and based on condensation, adsorption, and sublimation. Fig. 1 illustrates the volatile cycles on Mars, showing the different volatile reservoirs and interactions between them, not all of which are likely to be currently active.

Results from space missions have measured the isotopic composition of species in the martian atmosphere and lithosphere (Table 2). The distribution of volatiles in the lithosphere is varied: they can occur as part of the structure of primary mineral grains (e.g., apatite or amphibole), be trapped within vesicles or fluid inclusions within primary silicates, be incorporated into secondary minerals during weathering (e.g., clay minerals) or deposited during diagenesis (e.g., carbonates, sulfates). When combined with results from analysis of volatiles in martian meteorites, it is possible to start to put together a framework for volatile cycling on Mars, although with large error bars and gaps in information.

The chronology of interactions between volatile reservoirs on Mars almost certainly rests on the timing and extent of degassing of the martian interior as it cooled and solidified (45). Volatile species would be transferred from the crust (and deeper interior) into the atmosphere, for subsequent dissolution into surface fluids and precipitation as salts plus secondary minerals produced by weathering (46). Magmatic activity would drive subsurface hydrothermal activity, also leading to production of secondary minerals (47). Consensus has it that (at least sporadically) Mars' earliest atmosphere was much thicker than it is currently, allowing water to be stable at the surface (48, 49). When and how this atmosphere was lost has been modeled: hydrodynamic escape to space and/or sequestration in the crust of much of the primordial atmosphere probably occurred by ~400 Ma after initial aggregation of the planet (7, 8, 50, 51). However, since there are clearly fluvially produced landforms present in the early Amazonian, a sufficiently dense atmosphere for water to be stable was present, probably intermittently, for at least a further 2000 Ma.
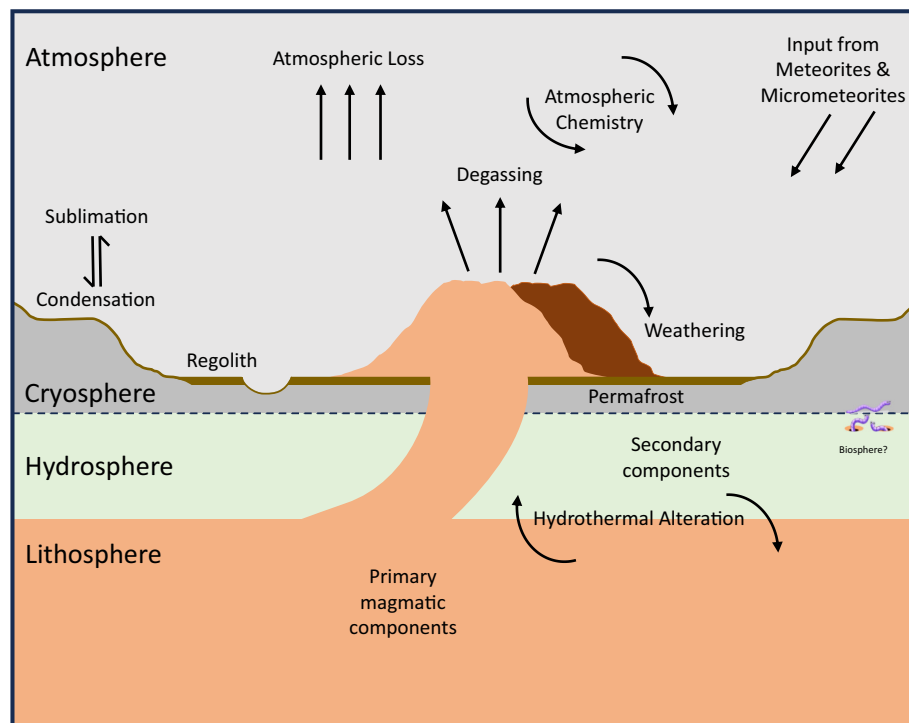
Fig. 1. Schematic illustration of the major volatile reservoirs that have been operational at different times during Mars' history. The arrows indicate interactions between the reservoirs.

Spectroscopic observations of Mars' surface have shown extensive regions where rocks containing hydrous minerals outcrop [e.g., Mawrth Vallis, (52); Jezero Crater, (53)]. Their precise mode of formation is not known: although they are evidently water-lain sediments, there are several different mechanisms that might have produced them, including surface weathering, subsurface groundwater alteration, or hydrothermal alteration at depth (45, 46, 54–57). Age-dating of hydrous minerals in martian meteorites indicates that at least some of the phyllosilicates were formed as recently as ~650 Ma ago (58–60), although the possibility of subsequent exchange with a later reservoir (atmosphere or hydrosphere) might obscure their true age. Nonetheless, data from MSL have confirmed the findings from meteorites, that aqueous alteration may have persisted longer in Mars history than previously believed, with ages of <2 Ga derived from jarosite (61).

Even more problematic than the timing and mechanisms of formation of hydrous minerals is the equivalent cycle for carbonates. For many years, there have been debates about the "missing carbonates"—calculations based on models of the ancient atmosphere predicted that there should be widespread deposits across Mars (62, 63). They have been observed from orbit in limited regions (64, 65), as well as in situ in rocks by the *Spirit* and *Perseverance* rovers (13, 14, 66) and by *Curiosity* (40, 43, 67) and as lofted dust in the atmosphere (68), but are less abundant than predicted. They are also known to occur in martian meteorites (69–72). As in the case for hydrous minerals, the formation mechanism of carbonates has important implications for the evolution of Mars' atmosphere (48). Return of carbonate-bearing samples from Jezero Crater could assist in a better understanding of the martian carbonate inventory.

Alongside consideration of the formation of hydrous minerals and carbonates comes investigation of chlorine- and sulfur-bearing species. Perchlorates and chlorides and sulfates and sulfides have been identified as components of the regolith by instruments on three landers [*Viking*, *Phoenix,* and *Curiosity*; (40)] and also in some of the sedimentary rocks collected by Perseverance (13, 14). One of the potential production mechanisms for both perchlorates and sulfates starts with UV-mediated photolysis of ozone in the atmosphere, a process characterized by mass-independent isotopic fractionation (73, 74). The subsequent stages of dissolution of oxychlorides and sulfur oxides in surface waters, followed by evaporite precipitation follow mass-dependent fractionation (42, 75, 76); the isotopic signatures of the two pathways are different and may be preserved in the final products. Measurements of the chlorine and sulfur isotopic compositions of Cl- and S-bearing salts in the martian surface are quite sparse (41, 42), so it has not yet been possible to evaluate the relative importance of the different fractionation mechanisms. Nonetheless, the presence of a variety of Cl- and S-bearing species in soils and rocks from all the sites investigated by landed spacecraft indicates that there is a rich chemistry of these volatiles to be unraveled. Analysis of materials collected at Jezero Crater should help to define the operation and complexity of the martian Cl and S cycles and how they interact with the movement of other species through the different volatile reservoirs.

Volatile-Bearing Components in Martian Meteorites

Measurements made at and on Mars by spacecraft are complemented by analysis of martian meteorites. Currently, almost 400 meteorites are recognized as being from Mars (https://www.lpi.usra.edu/meteor/); a complete description of the meteorites and their significance is given by Udry et al. (77). Evidence of their martian origin came following analysis of gases trapped in shock-produced glass in the Antarctic meteorite EET A79001 (78, 79), which was found to have the same elemental and isotopic composition as Mars' atmosphere as measured by the two *Viking* orbiters (31, 32). The martian origin of the meteorites formerly known as the SNCs is well established, even though they do not all contain trapped atmospheric gases. The genetic relationship between the different subgroups is recognized through the oxygen isotopic compositions of the primary magmatic minerals, which fall on a common mass-dependent fractionation line displaced from the terrestrial fractionation line [$\Delta^{17}O$ ~ +0.3‰; (80)].

All but one of the martian meteorites are igneous rocks, classified into five main subgroups with different mineralogies, petrogenesis, and ages (77). The Shergottite subgroup is believed to be produced by melting of the martian mantle (81–84), while the Nakhlite-Chassignite subgroups demonstrate evidence of a crustal component (85). The unique orthopyroxenite ALH 84001 is a slowly cooled cumulate that has experienced several shock events (86, 87). One meteorite (NWA 7034 and its pairs) is a regolith breccia composed of clasts of brecciated igneous material (88). Many

Table 2. Summary of the isotopic compositions of light element volatiles measured at Mars by spacecraft instrumentation

Mission	CO$_2$		H$_2$O		N	Cl	S	Refs.
	$\delta^{13}C$	$\delta^{18}O$	δD	$\delta^{18}O$	$\delta^{15}N$	$\delta^{37}Cl$	$\delta^{34}S$	
Atmosphere								
Viking	+23 ± 43	+7 ± 44			+680 ± 70			31 and 32
Curiosity	+46 ± 4	+48 ± 5	4,950 ± 1,080		+600 ± 60			33–35
ExoMars-TGO	59 ± 23		0 to +5,000			−6 ± 78		36 and 37
	−3 ± 37	−29 ± 38	3,500 ± 300	−100 to +300				38 and 39
Surface								
Viking	+0 ± 50	+0 ± 50						32
Curiosity (Various sites in Gale Crater)								
		−6 to +20	+3,900 to +7,000				+0 ± 10	40
	−25 to +56	−61 to +64				−51 to −1	−47 to +28	41–43
Oxygen				~+40				43
Methane	−137 to +22							44

All isotopic compositions are in ‰. Errors, when quoted, are as given by the authors.

of the meteorites are shocked, with feldspars transformed to maskelynite (89, 90). Volatile-bearing components in martian meteorites originate from the reservoirs described in the previous section, and include primary magmatic minerals (lithosphere), secondary phases produced by alteration (hydrosphere, atmosphere) and tertiary phases produced by shock (atmosphere). Volatile species may occur within fluid-inclusions or melt-residues, as primary species exsolved along grain boundaries, as part of a crystallographic structure or enclosed within the silicate lattice.

Primary Components. The primary components in martian meteorites are minerals that crystallized from magma. These rock-forming minerals (olivine, clinopyroxene, feldspar) are nominally anhydrous, i.e., they do not contain water as part of their crystallographic structure. But it has been known for some time that nominally anhydrous minerals (NAMs) can contain significant quantities of volatiles, especially water and chlorine, up to a few weight percent in some cases (91). Precise measurement of the abundance and isotopic composition of water in NAMs can be achieved using an ion microprobe; results have been variable. Assimilation of martian crustal water and/or exchange with the martian atmosphere are mechanisms that might induce heterogeneity; terrestrial contamination during sample processing is another. Interpretations of the results suggest that water in the martian mantle is isotopically light with δD of between around –100‰ and +275‰ (92–94). This range is similar to δD of the terrestrial mantle, implying that Mars and Earth formed from similar starting materials (91–93).

Primary magmatic minerals in some of the meteorites contain melt pockets with volatile-rich late-stage accessory minerals, such as the amphibole kaersutite (95–97). These phases have the capacity to incorporate several weight percent water (as OH), fluorine and chlorine in their structures, as well as (less commonly) S-, C-, and N-bearing species. The hydrogen isotopic compositions of water in these minerals are variable, ranging from about –250‰ to +4,500‰ (92–94, 98–100). Many authors conclude that the variation results from different extents of mixing between isotopically light water from the mantle with D-enriched water from the atmosphere, but there have been suggestions that this mixing is insufficient to explain the variation, and that the mantle itself is heterogeneous in hydrogen isotopic composition (101, 102). Measurement of D/H in primary magmatic minerals in the returned basaltic materials should be an immediate test of mantle heterogeneity.

There have been several measurements of magmatic carbon in martian meteorites. The amounts of carbon are low and appear to be isotopically light, with $\delta^{13}C$ around –30 to –20‰ (103–108). This is much more ^{13}C-depleted than carbon in Earth's mantle [$\delta^{13}C$ around –3‰; (109)]. Recognition of primary magmatic nitrogen in martian meteorites is equally difficult: results from stepped pyrolysis or combustion have given a range of values with $\delta^{15}N$ around –35 to 0‰ (104, 110–113). More recent measurements by ion microprobe recorded a similar isotopic composition [$\delta^{15}N$ of 0 ± 30‰ (114)]. Sulfur is abundant on the martian surface (115, 116) and analyses of minerals in martian meteorites show that crustal assimilation has been an important process in defining their sulfur isotopic compositions (117–120). Where sulfur data have been acquired on mainly magmatic phases, they have a $\delta^{34}S$ of –1.4‰ (119), which is close to that of Earth's mantle [$\delta^{34}S$ of –1.28 ± 0.22‰; (121)]. Chlorine is also abundant on the martian surface and, like sulfur, it is not easy to determine an isotopic signature for primary magmatic chlorine. Values for $\delta^{37}Cl$ of between –0.6 to –0.3‰ have been recorded for chlorine in unshocked apatites, which may come closest to the isotopic composition of primitive martian chlorine (122, 123). This is very similar to the value measured in Mid-Ocean Ridge basalts for the composition of chlorine in Earth's mantle [$\delta^{37}Cl$ of –0.1 ± 0.4‰; (124)].

Secondary Components. As stated previously, secondary components in martian meteorites have been produced by alteration of the primary magmatic minerals and by deposition from fluids. There are no purely "sedimentary" rocks in the martian meteorite collection, although almost all of the specimens contain up to ~2 vol. % of secondary minerals (125, 126). The most altered of the martian meteorites are members of the nakhlite subgroup, a series of overlapping lava flows that crystallized around 1.3 Ga ago (127). The secondary minerals form complex assemblages of phyllosilicates, carbonates, sulfates, and chlorates, filling fractures within the primary minerals and forming interconnected and branching networks along which fluids might travel (128). The minerals are intermixed at the millimeter-scale and have oxygen isotopic compositions that are not in equilibrium with those of the primary magmatic silicates (75, 76, 129). The phyllosilicates tend to have high δD values, up to ~+3,500‰; oxygen and hydrogen isotopic data imply that the secondary minerals were formed by alteration from fluids that had exchanged with water in the martian atmosphere (92–94, 98–100). Age-dating of these alteration products in nakhlites suggests that they formed through succeeding waves of fluid alteration, some 600 Ma after the rocks solidified (58).

The main sink of carbon within martian meteorites is the variety of carbonates produced by secondary alteration: a mixture of siderite, calcite, dolomite, breunnerite, and magnesite in varying proportions. They are most abundant in nakhlites in which they have a carbon isotopic composition of $\delta^{13}C$ + 40 to + 50‰ and oxygen isotopic composition of $\delta^{18}O$ ~ +10 to +25‰ (69, 70, 72). Alteration in the unique orthopyroxenite, ALH 84001, has a different texture from the clay mineral-rich assemblages of the nakhlites. The meteorite is decorated throughout with millimeter-sized rosettes of carbonates with $\delta^{13}C$ ~ + 30 to +65‰ and $\delta^{18}O$ ~ 0 to +30‰ (71, 72, 130–133). The rosettes are layered, with separate layers having different cation compositions (134); carbon isotopic composition also varies with cation content (133). Phyllosilicates are almost completely absent. Like the meteorite, the carbonates are early Noachian in age, but at 3.9 Ga are slightly younger than their host (135). The unusual morphology of the carbonates in ALH 84001 led to the suggestion that they might have been produced by short-lived impact-driven episodes of metasomatism at temperatures >200 °C (136), although this theory has been discounted in favor of cooler surficial fluid alteration processes (temperatures <100 °C) (71, 72, 130, 137). Although the ages and morphology of the carbonate assemblages in nakhlites and ALH 84001 are very different, their carbon and oxygen isotopic compositions are similar, suggesting that they formed in similar environments of temperature and pH.

The isotopic composition of martian atmospheric CO_2 has been measured by several spacecraft (Table 2). The more precise data from SAM ($\delta^{13}C$ ~ + 46 ± 4‰ and $\delta^{18}O$ ~ + 48 ± 5‰) is close to the carbon isotopic composition of CO_2 trapped in martian meteorites (69) as well as the $\delta^{13}C$ and $\delta^{18}O$ of martian meteoritic carbonates (68–71, 129–132, 136). The implication of a common carbon isotopic composition for the martian atmosphere and carbonates is that atmospheric CO_2 was in equilibrium with the surface waters from which the carbonates were precipitated (69–72, 133). The age of the carbonates ranges from early Noachian [the rosettes in ALH 84001; (135)] to mid-Amazonian [nakhlites; (58)]. Trapping of atmospheric CO_2 in martian meteorites presumably occurred when the rocks were ejected from Mars' surface—which was as recently as 820 ka ago for EET

A79001 (138). The implication of these measurements is that there has been little change in the carbon isotopic composition of CO_2 in the atmosphere over a time period of >3.5 Ga. Knowledge of carbonate abundance and isotopic composition has provided the starting point for models of the original atmospheric CO_2 abundance, leading to estimates of the volume of water that could be stable under such an environment (139). As considered above, an unresolved issue is the lack of major carbonate outcrops on the surface of Mars. It is anticipated that the return of carbonate-bearing sedimentary rocks from Mars will provide additional information on the nature of the loss processes that influenced atmosphere–hydrosphere–lithosphere interactions during the Noachian.

Oxidized compounds of nitrogen, sulfur, and chlorine have also been detected in martian meteorites, although in much lower abundances than carbonates. The presence of nitrates with $\delta^{15}N$ of –11 to –8 ± 4‰ (140) and $\delta^{15}N$ of –10.5 ± 0.3‰ and $\delta^{18}O$ of +51.6 ± 0.7‰ (141) was inferred for samples of EET A79001 and Nakhla. Their presence has also been inferred at Gale Crater by SAM (142, 143). Martian atmospheric nitrogen is known to be enriched in ^{15}N (32, 35); the difference in $\delta^{15}N$ between the nitrates and atmospheric nitrogen suggests that production of nitrates was more complex than a simple interaction between atmosphere and lithosphere, possibly involving fixation of nitrogen by lightning strikes (144). The presence of nitrates in martian regolith could have important implications for the potential habitability of early Mars (144).

Sulfates in martian meteorites are isotopically much more variable than primary magmatic sulfur, with $\delta^{34}S$ between –10‰ and +15‰ (117–119). The two end-member compositions were ascribed to different processes: enrichment in ^{34}S from assimilation of sulfur species produced by photolysis reactions in the atmosphere, while depletion in ^{34}S was the result of hydrothermal alteration (117–119, 145). Analysis of sulfates at several locations in Gale Crater by SAM has shown the salts to have a similar (if slightly wider) range of sulfur isotopic composition than in the martian meteorites, with $\delta^{34}S$ between –47‰ and +28‰ (42, 43) (Table 2). Different generations of sulfates have also been identified in Jezero Crater (146)—analysis of returned samples could allow recognition of evidence for hydrothermal activity at the crater, again with associated implications for potentially habitable environments.

The chlorine isotopic compositions of secondary Cl-bearing salts in martian meteorites are interpreted as reflecting a mix of a lighter, more primitive mantle reservoir with a secondary, isotopically heavier reservoir (probably the atmosphere) with $\delta^{37}Cl$ = ~+9‰ (147–149). Interactions between crustal fluids and atmospheric chlorinated species have the potential to preserve a signature of the different processes occurring (or having occurred) in the atmosphere (magmatic degassing, atmospheric loss, and atmospheric chemistry (including molecules and free radicals produced by photolysis). In order to unravel such a history, high precision analyses will be required at high spatial resolution, to distinguish between, e.g., the coats and cores of mineral grains.

Samples in the Three Forks Cache

By the end of 2022, the Perseverance rover had completed its primary mission to explore the floor of Jezero Crater and the western delta front. During the (martian) year of its operation, the rover collected 17 samples from different locations across the crater, focusing on the edge of the delta which occupied part of the crater's western side (13, 14). The strategy for return of the sample collection to Earth was to leave a cache of representative samples at a single location (Three Forks) in Jezero Crater, while the rover continued to explore beyond the lip of the crater collecting additional samples. The sample tubes would be collected for return to Earth by a later mission. An international workshop was held in September 2022 to consider the inventory of material collected by Perseverance, in order to decide which samples would be left in the cache and which should be carried onward. The outcome of the workshop and the decision-making process followed was published in mid-2023 (150). Table 3 lists the 10 samples that form the cache deposited at the Three Forks location in Jezero Crater; the information in the Table was drawn from Farley and Stack (13, 14), with stratigraphic classification from Stack et al. (151). Herd et al. (152) have a more complete description of all the samples collected by Perseverance, not solely those in the cache.

Understanding the role of volatiles in the evolution of Mars was Objective 4 of the iMOST report (10): "*Constrain the inventory of martian volatiles as a function of geologic time and determine the ways in which these volatiles have interacted with Mars as a geologic system*" (10); it was broken down into four subobjectives which are summarized in Table 1. All four of the subobjectives can probably be met with the cached samples, although subobjective 4D ("*assessment of temporal variations in the martian atmosphere*") will be dependent on the age range of components within the sedimentary rocks, since only one sample of atmosphere has currently been deposited in the cache. In the following sections, linkages are made between the Investigation Strategies (IS) and potential measurements to be made on the returned samples in support of Objective 4. A much more complete relationship between Objectives, Investigation Strategies, and specific samples is contained in the Sample Science Traceability Matrix of Czaja et al. (150).

Leaving aside the search for biological signatures, it could be argued that the most important initial measurement to be made on the returned samples is of their age (157). This will not only give a detailed chronology of Jezero Crater, but will also calibrate the stratigraphy of Mars, yielding a more extensive regional (possibly global) timeline for crustal processes. Isotopic analysis of volatiles in martian meteorites, coupled with data from space instrumentation has given us a framework for constructing the pathways by which volatile species exchange between the different reservoirs. Knowing the specific chronology of returned material and the field locations from which it was recovered will provide a context for a much more detailed understanding of how volatile compositions have changed with time. Once the ages of the different returned samples (and individual mineral components within them) have been determined, detailed analysis of the volatiles in each sample will allow determination of the extent of current interactions between the different volatile reservoirs. For example, comparison of the isotopic composition of CO_2 in the atmospheric sample with that of carbonates in the sedimentary rocks could help to constrain the mechanism and temperature of carbonate formation.

Potential Returned Sample Science from Igneous Rocks

Four of the samples in the Three Forks cache were collected as part of the Crater Floor campaign and have been identified as igneous rocks with various degrees of weathering (13). Two of the samples (Coulettes and Malay) are cumulates from the Séitah Formation; they may be part of a thick lava flow or lava lake (154). The other two samples in the cache are basalts. Montdenier is from the Lower and Atsah from the Upper Máaz Formation (153). They overlie the cumulates of the Séitah Formation and are assumed to be younger (13).

Table 3. Samples cached in the Three Forks depot by *Perseverance*

Name	Location	Rock type
Igneous Specimens (Collected during the Crater Floor Campaign)		
Montdenier	Artuby Ridge; Lower Máaz Formation	Minimally altered basalt or basaltic sst (153)
Coulettes	Brac Outcrop, Mid (?) Séítah Formation	Medium- to coarse-grained poikilitic olivine cumulate; thick lava flow or lava lake (154)
Malay	Issole Outcrop; Upper Séítah Formation	Medium- to coarse-grained poikilitic olivine cumulate; thick lava flow or lava lake (154)
Atsah	Individual rock (Sid); Upper Máaz formation	Andesitic basalt (153)
Sedimentary Specimens (Collected during the Delta Front Campaign)		
Skyland	Skinner Ridge, Hawksbill Gap (Shenandoah Formation)	Fine to medium-grained sandstone. Deltaic (155)
Bearwallow	Wildcat Ridge, Hawksbill Gap (Shenandoah Formation)	Sulfate-bearing coarse mudstone. Lacustrine (155) or subaerial (156)
Shuyak	Amalik Outcrop, Cape Nukshak (Shenandoah Formation)	Olivine-bearing coarse mudstone. Fluvial (155)
Regolith sample (Collected during the Delta Front Campaign)		
Crosswind Lake	Observation Mountain, Cape Nukshak	Mainly fine-grained particles but coarser particles are inferred to be present.
Atmosphere sample (Collected during the Crater Floor Campaign)		
Roubion		Serendipitous
Witness Tube: (Processed during the Delta Front Campaign)		
WB3		The second of the ACA WTA to be processed

Studies of the volatile content of minerals in unaltered Noachian-aged igneous samples can provide clues to the bulk volatile content of Mars (IS 4A); the successful collection of such material from the floor of Jezero Crater opens the door to a range of important findings based on volatile analysis. Determination of the abundance and isotopic composition of volatiles in Noachian-aged NAMs and phosphates provides key constraints on Mars' primary magmatic signature. The oxygen isotopic composition of the major rock-forming minerals is diagnostic of the source materials from which they have crystallized—in this case, the interior of Mars. Measurement of this parameter in primary minerals would be the ultimate piece of evidence that martian meteorites are indeed from Mars. More notably, any deviation from mass-dependent fractionation in secondary components would indicate assimilation of material from a different source, (e.g., the atmosphere) prior to solidification of the magma.

Isotopic variability, especially in hydrogen, may help to infer the homogeneity, or otherwise of the lithospheric reservoir (101). When coupled with D/H analysis of trace water vapor in the current martian atmosphere, the results should inform calculations of the contributions the different species made to Mars' earliest atmosphere (IS 4C). Return of igneous rocks also provides an opportunity to search for trapped volatile species—gases present in vesicles, fluid inclusions, or melt inclusions (158). These are likely to be primary, and because they are protected within the crystal lattice from exchange with the external environment, also have the potential to preserve the composition of the original magmatic gases which subsequently degassed to form the early martian atmosphere (IS 4A). It is important to determine which gases are present—is carbon present as CO_2 as in the current atmosphere, or does it occur as CO or CH_4? The same for hydrogen, nitrogen, sulfur, and chlorine species: their identification and isotopic composition in inclusions in primary magmatic minerals should reflect the redox state of the atmosphere (45). This should enable evaluation of the possible effect of ozone production on the chemical reactions that were occurring (76), for comparison with the current atmosphere (IS 4B). Sample analysis of rocks of

different ages could then be used to constrain the evolution of the martian atmosphere and date more precisely periods of climate change.

Potential Returned Sample Science from Sedimentary Rocks

Sedimentary rocks, which may be altered igneous rocks or chemical sediments, are rich in the volatiles of interest. Detrital grains of primary magmatic silicates can be dated to determine the age of their source rocks. The oxygen isotopic composition of these detrital grains would then yield information about their source rocks, for comparison with the igneous rocks described above (IS 4A). The relatively closely spaced locations from which the cached specimens were collected do not necessarily imply that the sedimentary materials were sourced from the igneous rocks that form the crater floor—the drainage basin that feeds the delta comprises two main channels with a network of tributaries that have a catchment area of several thousands of square kilometers (159). As outlined in the previous section, grains with an igneous origin often contain gases trapped in vesicles and fluid inclusions; if the detrital grains in the sedimentary rocks have different ages, they may be sampling the martian atmosphere at different times (and climates) (IS 4B, 4C).

The second set of materials that host volatiles in the sedimentary samples are the secondary minerals produced by alteration or weathering, specifically the hydrous silicates (clay minerals or phyllosilicates) that form from the primary minerals. Phyllosilicates contain water bound within the silicate lattice (both as the hydroxyl ion and as molecular water) and also adsorbed onto mineral surfaces (as water). Molecules in the latter site are less tightly held than in the former and so are more susceptible to exchange with the external environment. Careful analysis of O and H in phyllosilicates, when coupled with equivalent analyses on primary silicates, should provide information on the alteration processes that produced the secondary minerals, including the isotopic composition of the fluids involved. Knowing the ages of

the primary and secondary minerals could constrain the timeline of alteration (IS 4B).

The third set of materials of interest for their volatile compositions are the chemical sediments: carbonates, sulfates and sulfides, nitrates, perchlorates, and chlorides. These are minerals produced by deposition from surface or near-surface fluids. There are at least two time periods when these minerals could be produced: early, from magmatic fluids, or much later, by subsurface fluid alteration. Carbonates and sulfates often occur as matrix cements; dating of the minerals could yield the time of diagenesis; the isotopic composition of cements of different ages should show how temperatures and fluid composition had varied with time, potentially highlighting episodes where the ancient climate changed (IS 4B, 4C). It is important to determine the chemical or elemental composition of minerals hosting or composed of volatile species. For example, the composition of carbonates (calcite, dolomite, magnesite, etc.) is related to the composition of the fluid from which they were precipitated. Changes in cation composition could represent fluctuations in fluid composition, signifying different deposition regimes (fluvial to lacustrine, for example).

Three of the samples deposited by *Perseverance* are identified as sedimentary rocks from the Shenandoah Formation. Skyland is a fine- to medium-grained sandstone, possibly deltaic in origin (155). Bearwallow is a sulfate-bearing coarse mudstone, either lacustrine (155) or subaerial (156) in origin. Shuyak is an olivine-bearing coarse mudstone, possibly fluvial in origin (134). It is inferred from the relative stratigraphy of the three samples that Shuyak comes from lower in the sedimentary sequence than Bearwallow, with Skyland outcropping above Bearwallow. Assuming that the stratigraphy equates directly with chronology and that layers have not been overturned, then Shuyak is the oldest and Skyland the youngest of the three samples, although the actual age difference is unknown. The samples show a transition from fluvial, through lacustrine/subaerial to deltaic and descriptions of the cached materials indicate that they contain examples of the three sets of minerals that host volatiles (155, 156). Age-dating of equivalent components in the rocks should give a timeline for the deposition of the sediments (IS 4B, 4C). Isotopic and abundance measurements of the volatile components in the grains should yield the composition of the fluids from which the sediments were deposited, the composition of the atmosphere in equilibrium with the fluids and the temperature, salinity, oxidation state, and pH of the fluids. From this, it should be possible to see how the transition in depositional environment changed, with an inference that the atmosphere changed throughout the time period over which the sediments were laid down. Integrating the results with data from the (slightly older) igneous samples should show the relative amounts of gas added from volcanic emissions and lost through atmospheric loss processes (IS 4C).

Potential Returned Sample Science from a Regolith (and Dust) Sample

Much of the surface of Mars is covered by a layer of fine-grained wind-blown dust, a reservoir of the products of millions of years of erosional history, a mixture of all of the different rock types exposed at the surface (116). Chemical analyses of the soil by instruments on three different landers at three widely separated landing sites have shown that the dust is similar in composition over the planet's surface (160, 161). Therefore, this fine-grained component of the martian regolith offers insight into the physical processes of erosion and weathering that have operated throughout Mars' history. The Curiosity rover determined a cumulative grain size distribution of ~1 mm to ~1 cm for the soil at its landing site

in Gale Crater (162). The regolith sample collected by Perseverance and deposited in the Three Forks cache (Crosswind Lake) came from the Observation Mountain megaripple. The location was selected because of the size and immobility of the feature (163). The sample is reported to be a mixture of coarse-grains (up to ~5 mm diameter) with finer grains of sand and silt; airfall dust is also presumed to be present (14). The coarse-grains are likely to reflect the composition of the local bedrock and therefore provide an additional record of conditions and processes in Jezero Crater. They will sample a wider area than is represented by the drill cores—although the dust mixed in with the regolith will be a globally averaged specimen.

Because regolith and dust samples are in contact with the atmosphere, they could preserve a record of interactions between the atmosphere and Mars' surface (IS 4B, 4C). Regolith can act as a sink for the products of atmospheric chemistry; it might also act as a catalyst by providing a substrate for reactions to proceed. Isotopic signatures of reactants (e.g., ^{13}C-enriched CO_2; D-enriched water, etc.) may then be preserved in different minerals.

Potential Returned Sample Science from a Sample of the Atmosphere (and Cryosphere)

Changes in the martian climate—from warm and wet, to cold with scattered showers, and now cold and dry, are closely coupled to changes in the martian atmosphere. There is one sample in the Three Forks cache that is specifically designated to be a sample of atmosphere (Roubion); however, each sample tube will contain a small volume of atmosphere which is assumed to be in chemical and isotopic equilibrium with the material within. Collection and analysis of these individual gas volumes could yield information on the variability of atmospheric composition (IS 4D) across the ~470 Sols over which they were collected (13, 14).

Although magmatic outgassing as the planet cooled was the main source of atmospheric gases, the presence of chemical disequilibrium in the contemporary atmosphere indicates continued input and removal of gases produced by physical or chemical processes. One of the main mechanisms for driving chemical reactions in Mars' atmosphere is that of the breakdown of atmospheric species (especially water vapor and CO_2) by UV solar radiation, forming ozone (O_3) and oxy-hydrogen free radicals (HO•, HO$_2$•, etc.) which then go on to react further, producing a variety of different molecules. Eventually, interaction with surface fluids may lead to formation of secondary minerals. Photolytic degradation is non-mass-dependent, and so can result in production of carbonates, sulfates, perchlorates, etc., with isotopic compositions that are not in equilibrium with that of the fluid from which they have been precipitated. It is possible that additional high precision analyses at high spatial resolution of such minerals in returned samples might be able to determine whether there is any signature of mass-independent photolysis processes preserved in the secondary salts.

It is also possible that the disequilibrium between species might be a potential biosignature. The presence of methane in Mars' atmosphere is currently contested: the NOMAD instrument on the Mars TGO has consistently reported no methane in the upper atmosphere (164, 165), while the SAM instrument suite on the Curiosity rover has found seasonal and diurnal release of pulses of methane (166, 167). Since methane is potentially a significant biosignature, it is important to determine its abundance and H and C isotopic compositions, so that a better understanding of the methane cycle is gained—is the methane present at the surface from secondary weathering (serpentinization of olivine)? Or is it from a biosphere (Objective 2)?

As indicated in the figure, Mars' cryosphere, represented by the northern and southern icecaps, is in constant contact with the atmosphere. The icecaps are observed to grow and shrink with Mars' seasons, changing the composition of the atmosphere—a process which has continued throught Mars' evolution. On Earth, ice cores have been found to hold valuable records of climate change—one can assume that the same would be true of Mars. No current mission to Mars is planned which would return an ice core from either a polar cap or from deep within the regolith. But such a sample would be important in helping to complete knowledge of volatile cycling between reservoirs on Mars.

Summary

In order to reconstruct the history of water on Mars and how this relates to changes in martian climate over the past 4.6 billion years, it is essential to have an understanding of the different reservoirs present and how volatile species cycle through them. To build as full a picture as possible, we need to know which species are present, their absolute and relative abundances and their isotopic compositions, and how these might vary with season (short term) and martian obliquity (long term). It is also necessary to understand the physical and chemical processes which affect production and loss of the volatiles (including magmatic degassing, atmospheric stripping, weathering, and chemical reactions). Only then will we be able piece together the evolution of water and other volatiles on Mars, and hence detect any potential trace biological signatures present.

At present, our knowledge of Mars' volatile budget relies on analysis of the atmosphere and surface by instrumentation on orbiters, landers, and rovers, complemented by direct measurement of martian meteorites. Modeling of aqueous and magmatic activity based on fluvial and volcanic features, linked with scenarios for

how Mars' atmosphere has changed since the planet first formed, has enabled estimates for the volatile budget in the past. The figures are lacking in detail because of incomplete sampling: we are able to make an estimate of the original volatile content of the martian interior, but it relies on a single Noachian-aged specimen of unknown martian provenance, ALH 84001, which has experienced both martian and terrestrial weathering.

Although there have been great advances in spacecraft instrumentation and the range of analyses that are possible on Mars, there are still limitations in sample preparation techniques that preclude use of some of the most useful methods employed to analyze rock samples. For example, high precision measurement of the isotopic compositions of rocks and minerals on Mars' surface has not yet been possible, because of the complex nature of the preparation and analysis procedures required (e.g., fluorination of silicates for measurement of oxygen isotopes; polishing to a flat surface for ion microprobe analyses, etc.). It is only with the return of samples collected from a known area on Mars that we will have the required geological context to couple with precise compositional measurements that will enable a more thorough understanding of martian volatile history.

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