Combining meteorites and missions to explore Mars

Timothy J. McCoy[1], Catherine M. Corrigan, and Christopher D. K. Herd[2]

Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution, 10th and Constitution Avenues NW, Washington, DC 20560-0119

Edited by Mark H. Thiemens, University of California San Diego, La Jolla, CA, and approved August 24, 2011 (received for review March 30, 2011)

Laboratory studies of meteorites and robotic exploration of Mars reveal scant atmosphere, no evidence of plate tectonics, past evidence for abundant water, and a protracted igneous evolution. Despite indirect hints, direct evidence of a martian origin came with the discovery of trapped atmospheric gases in one meteorite. Since then, the study of martian meteorites and findings from missions have been linked. Although the meteorite source locations are unknown, impact ejection modeling and spectral mapping of Mars suggest derivation from small craters in terrains of Amazonian to Hesperian age. Whereas most martian meteorites are young (<1.3 Ga), the spread of whole rock isotopic compositions results from crystallization of a magma ocean >4.5 Ga and formation of enriched and depleted reservoirs. However, the history inferred from martian meteorites conflicts with results from recent Mars missions, calling into doubt whether the igneous histor y inferred from the meteorites is applicable to Mars as a whole. Allan Hills 84001 dates to 4.09 Ga and contains fluid-deposited carbonates. Accompanying debate about the mechanism and temperature of origin of the carbonates came several features suggestive of past microbial life in the carbonates. Although highly disputed, the suggestion spurred interest in habitable extreme environments on Earth and throughout the Solar System. A flotilla of subsequent spacecraft has redefined Mars from a volcanic planet to a hydrologically active planet that may have harbored life. Understanding the history and habitability of Mars depends on understanding the coupling of the atmosphere, surface, and subsurface. Sample return that brings back direct evidence from these diverse reservoirs is essential.

Laboratory studies of over 50 meteorites derived from Mars, plus data collected by numerous orbital and landed spacecraft, paint a picture of a rocky planet that evolved in a fundamentally different way than Earth. It has scant atmosphere, no evidence of crustal recycling (plate tectonics), evidence for copious amounts of water that—if still present—is frozen and largely underground, and crustal ages ranging from approximately 4.0 Ga to no more than 180 Ma.

Since its inception, the study of martian meteorites has been intimately linked to the exploration of Mars by orbital and landed spacecraft. The very recognition of martian meteorites was enabled by our exploration of Mars. From that initial stage, both the number of martian meteorites and missions to Mars has increased dramatically, unveiling fundamental insights into the history of Mars and posing additional questions, many driven by ground- and space-based technological advances. In most respects, the studies of martian meteorites and martian rocks and terrains from missions have been highly complementary, with each asking questions and framing answers for the other. Among the most interesting areas of exploration—driven by a controversial finding from a martian meteorite—is the search for ancient or extant life. Achieving this goal requires a better understanding of linkages between the interior, crust, and atmosphere that have driven, and may continue to drive, the evolution of the planet and, ultimately, an increasingly necessary (if elusive) Mars sample return mission. In this paper, we discuss how martian meteorites, when coupled with Mars missions, have elucidated these important reservoirs. We argue that Mars sample return—which is widely accepted as the highest priority for Mars exploration—can and must contribute to our understanding of all of these reservoirs if we are to understand Mars as a system.

Among the meteorites now recognized as martian, the first to be recovered fell October 3, 1815 in Chassigny, France, only 20 y after meteorites were recognized to have an extraterrestrial origin. In hindsight, hints of a martian origin were available from 1950, but final recognition awaited a remarkable finding in 1983. By that time, it was recognized that a duo of basaltic meteorites, Shergotty and Zagami, differed from the abundant basaltic eucrite meteorites. This duo (later joined by other meteorites to be called shergottites after the archetypal meteorite) was linked to the pyroxenitic nakhlites and the olivine-rich dunite Chassigny through a common oxygen isotopic signature (1). The common parent body to these disparate meteorites clearly produced a diverse range of igneous lithologies. Further, all of these meteorites shared apparently young ages of 1.3 Ga or less (2), either requiring resetting during heating in a later impact event or young crystallization ages and a planet-sized body to explain recent, near-surface igneous activity. Among the earliest suggestions of a martian origin was that of McSween and Stolper (3) based on similarities between the bulk compositions of these meteorites and soil compositions measured by the Viking lander. Direct evidence for a martian origin came with the discovery of high ratios of $^{40}Ar/^{36}Ar$ and $^{129}Xe/^{132}Xe$ in trapped gases in shock-altered phases of the Antarctic meteorite Elephant Moraine A79001 that closely resembled martian atmosphere measured by the Viking lander (4). This remarkable discovery set the stage for three decades of investigations about Mars that, like the initial findings, coupled laboratory analyses of these meteorites with observations from spacecraft. This approach recently came full circle with the discovery on Meridiani Planum by the Mars Exploration Rover Opportunity of an isolated rock whose textural, mineralogical and chemical properties are very similar to that of certain basaltic shergottites, including Elephant Moraine (EET) A79001 (5) (Fig. 1).

Among the earliest questions was how these meteorites reached Earth and where they originated on Mars. Initial skepticism about a martian origin centered on the shock pressures required for impact ejection, which should have produced complete melting of the ejecta. Proof that meteorites could be ejected unmelted from large bodies came with the discovery of the Allan Hills (ALH) A81005 Antarctic meteorite and the recognition of its lunar origin (6). Early analytical solutions to ejecting material as spallation blocks indicated that craters of the order of 10–15 km were required. Later workers called for a single, either very large [e.g., 200 km; (7)] or oblique (8) impact event on a geologically diverse terrain with ejection of multimeter sized blocks and subsequent collisions in space to explain the diverse cosmic-ray exposure ages. As the number of recognized martian meteorites increased, these latter models became increasingly

Author contributions: T.J.M. designed research; T.J.M., C.M.C., and C.D.K.H. performed research; and T.J.M., C.M.C., and C.D.K.H. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

[1]To whom correspondence should be addressed. E-mail: mccoyt@si.edu.

[2]Permanent address: Department of Earth and Atmospheric Sciences,University of Alberta, 1–26 Earth Sciences Building, Edmonton, AB, Canada T6G 2E3.

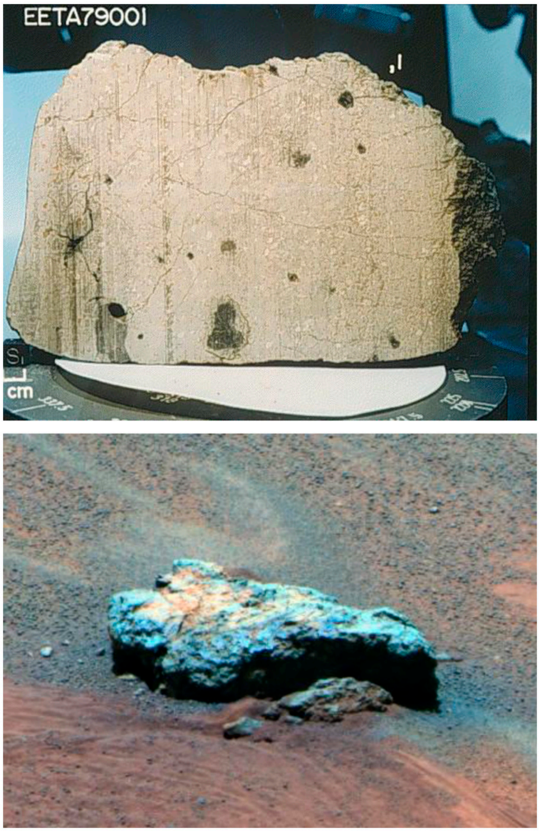

Fig. 1. Images of martian meteorite Elephant Moraine (EET) A79001 (above) and martian rock Bounce Rock (fasle color; below). Dark patches in EET A79001 are shock-melt pockets containing trapped martian atmosphere. Scale cube above is 1 cm and length of Bounce Rock is approximately 40 cm. Images courtesy of NASA/Johnson Space Center (EET A79001) and NASA/Jet Propulsion Laboratory (Bounce Rock).

untenable. The most recent work (9) combines petrologic determinations of peak shock pressures, evidence of six distinct cosmic-ray exposure clusters and inferred source craters, calculated transit times and probabilities for martian ejecta, and residence times for meteorites on Earth as tests for comparison with numerical modeling of crater ejecta, concluding that numerous smaller craters, ranging from 3 km in young terrains to 20 km in ancient terrains with thick regolith, likely ejected the martian meteorites.

Whereas this combination of laboratory-based constraints on martian meteorite origins and numerical modeling of ejection and delivery mechanisms points to numerous small craters, identification of those craters and their associated terrains remains an elusive goal. Recent attempts to identify possible source craters include the work of Hamilton et al. (10) and Lang et al. (11). Hamilton et al. (10) modeled the thermal emission spectra (approximately $1{,}400 - 200\ \mathrm{cm}^{-1}$) collected by the Mars Global Surveyor Thermal Emission Spectrometer using laboratory spectra of six martian meteorites, atmosphere and previously defined spectral surface types to identify possible ejection sites for these meteorites. No sites matching the basaltic shergottites were identified, although several potential sites for the intrusive meteorites ALH A77005, Chassigny and ALH 84001 were identified near the highlands-lowlands boundary and near Argyre and Hellas basins. Lang et al. (11) likewise could not conclusively identify sites matching the basaltic shergottites from Tharsis. The Argyre and Hellas sites date from the Amazonian to Hesperian period of martian history, which could suggest that Noachian terrain (>3.9 Ga) has not been sampled, although the absolute age of the Hesperian–Noachian boundary is highly uncertain. The lack of geologic context coupled with the apparent bias toward ejection of martian meteorites from younger geologic units is one of the most significant limitations in coupling martian meteorite and spacecraft-based studies to understand the history of Mars. With the availability of visible to near-infrared data from the OMEGA spectrometer on Mars Express, revisiting this exercise to identify possible source regions for the shergottites might prove productive.

In spite of the lack of "field context," detailed studies of these samples have yielded insights into the geologic evolution of Mars. Much of the first geochemical modeling of the martian interior derived from the analysis of radiogenic isotopes for geochronology. Results for the shergottites showed a significant and large variation in initial isotopic ratio, especially for Sr (12), and it was apparent that the initial $^{87}\mathrm{Rb}/^{86}\mathrm{Sr}$ and $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ values for meteorite whole rock samples plot on a line with a slope corresponding to 4.5 Ga (13). This led to the postulation that 4.5 Ga was the true crystallization age of the shergottites, and that approximately 180 Ma ages obtained by mineral separate Rb–Sr and Sm–Nd reflected resetting by impact metamorphism—a genuine concern because each meteorite experienced at least one impact event, associated with its liberation from Mars, with peak shock pressures in the range of 5–55 GPa and postshock heating up to 1,000 °C (14). This view was further supported by $^{39}\mathrm{Ar}$–$^{40}\mathrm{Ar}$ (giving ages of >250 Ma) and U–Th–Pb results (2). Following arguments that shock metamorphism is unable to fully reset isochrons (2, 12), an alternative view was proposed to explain the 4.5 Ga apparent age in which the spread of whole rock isotopic compositions is attributed to mantle source characteristics or mixing (13, 15). In this scenario, isotopically enriched and depleted reservoirs are formed by 4.51 Ga (15), and remain unmixed and undisturbed until the melting event that makes a shergottite magma. The geochemical characteristics of a shergottite are dictated by which reservoir, or combination of reservoirs, is involved in melting. In practice, the shergottites cluster into three distinct geochemical groups on the basis of their enrichment and depletion in Rb–Sr, Sm–Nd, and rare earth elements (REEs) (Fig. 2), despite being petrologically similar across groups. The range of time-integrated isotopic composition (e.g., $\varepsilon^{143}{}_{\mathrm{Nd}}$) among the shergottites is very large compared to basaltic rocks from Earth, suggesting long-term (4.5 Ga) separation of the enriched and depleted reservoirs with mixing only taking place just prior to magma genesis.

Although much information has been gleaned from the martian meteorites in terms of the geologic evolution of Mars, it is apparent that these meteorites are not representative of the bulk of the rocks at the martian surface (16). In spite of attempts to link martian meteorites to their parent impact craters, the stratigraphic context of these samples is not known. All but one martian meteorite (ALH 84001) have ages ≤1.3 Ga. There does not appear to be a sample of the crust of Mars that resulted from the approximately 4.5 Ga differentiation of the silicate portion of Mars within the martian meteorite suite. The overrepresentation of young martian basalts among martian meteorites has led some workers to revisit the idea that the true crystallization of shergottites is ancient and to reinterpret young mineral separate ages as due to resetting (17). However, a mechanism of preferential resetting of all chronometers save Pb–Pb, either impact metamorphism or impact-induced metasomatism by acidic solutions (17), is not supported by petrographic observations of shergottites (e.g., ref. 19) or theoretical and experimental considerations (12). The delivery of martian rocks to Earth is inherently biased toward younger, more coherent (igneous) rocks; older rocks representing primitive martian crust and weakened by impacts and aqueous alteration are likely discriminated against in the launch process (19 and references therein).

The differentiation of the silicate portion of Mars is called upon to form the enriched and depleted reservoirs. Both rapid

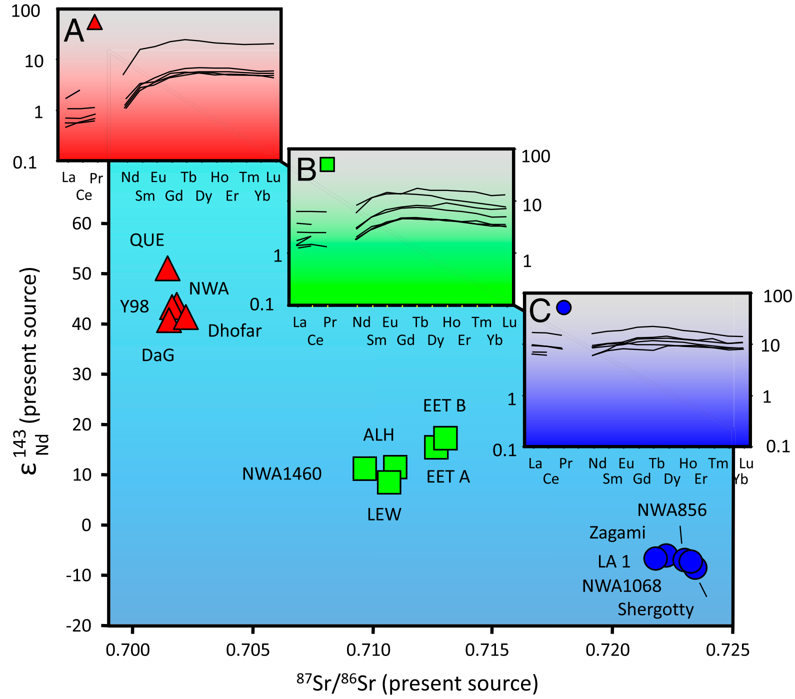

Fig. 2. Present-day $^{87}Sr/^{86}Sr$-ε^{143}_{Nd} plot of shergottite source regions illustrating three distinct suites of martian meteorites, including QUE 94201 (QUE), Yamato 980459 (Y98), Dar al Gani 476 (DaG), Northwest Africa 1195 (NWA), EETA79001 lithologies A and B (EET A, EET B), ALH 77005 (ALH), LEW 88516 (LEW), Los Angeles (LA), and others (as noted). Representative REE patterns for each group are shown in the *Inset*. Modified from ref. 18.

production of a primitive, early martian crust by partial melting of the mantle, and crystallization (and subsequent overturn) of a magma ocean have been proposed as mechanisms to produce these reservoirs (13, 20, 21). In the partial melting scenario, the enriched reservoir is the primitive crust and the mantle is the depleted counterpart. In the latter case, the last dregs of crystallization of a magma ocean highly enriched in incompatible elements comprise the enriched portion, and the cumulate mantle is the depleted counterpart (21, 22). Either scenario may explain the observed variations in geochemical characteristics; however, each implies a dramatically different petrogenesis for the enriched shergottites. In both scenarios melting of depleted mantle produces a depleted melt that, if left untouched, erupts at the martian surface and preserves its depleted characteristics. In the primitive crust scenario, the parent melt assimilates enriched crust before eruption. In contrast, the magma ocean scenario involves the melting of mantle reservoirs with either enriched or depleted characteristics; an enriched shergottite forms from the melting of an enriched mantle source. Problems exist with both models. However, a correlation between redox state (oxygen fugacity, fO_2) and REE or radiogenic isotopic composition (23, 24) is best interpreted in the context of mantle source variation (25), primarily because there is no reasonable mechanism to simultaneously affect both long-term incompatible element enrichment and higher redox state.

Fig. 3. A 176.3 gram sample of martian meteorite Allan Hills 84001. *Inset* photo is approximately 200 micrometers in width and show a compound carbonate rosette. ALH 84001 photo courtesy of the Smithsonian Institution. Carbonate image courtesy of NASA/Monica Brady, Natural History Museum, London.

The interior of Mars may have been a significant source of the water that was subsequently available for modification of the surface, through volcanic outgassing. However, the amount that was outgassed and retained depends on many factors, including the compositional mix of accreted materials, the efficacy of hydrodynamic escape and impact erosion, and the amount and efficiency of volcanic eruption and outgassing (26). Studies of martian meteorites have been used to attempt to constrain the latter. Although the meteorites themselves are very dry, containing on the order of <350 ppm bulk water (27), the preeruptive water contents of their magmas range up to approximately 2 wt%. The upper end of the range derives from experimental studies of the Shergotty intercumulus liquid composition (a proxy for its parent magma), which has only pigeonite on its liquidus at one bar (28). Liquidus cosaturation of pigeonite and augite, as indicated from petrography of the meteorite, can be achieved by the addition of 1.8 wt% H_2O (28). Alternatively, cosaturation can occur if an augite component is added to the Shergotty intercumulus liquid composition, obviating the need for dissolved water (29). Evidence of some amount of degassing of magmatic water is provided by reversed Li and B zoning trends in shergottite pyroxenes, which may be explained by removal of a Li- and B-bearing aqueous fluid upon eruption (30). However, boron zoning trends could not be reliably reproduced and the behavior of Li during crystallization or the effect of shock metamorphism on Li are poorly known (31). Magmatic inclusions containing kaersutite amphibole have been used to estimate preeruptive water contents of 1.4 wt% (32). However when measured directly, the kaersutite is hydrogen deficient (33), either because it crystallized in a H-poor environment (e.g., ref. 34), or as the result of loss due to impact shock. If primary, the low H content of the kaersutite yields preeruptive water contents of $<1{,}000$ ppm and mantle contents of 1–35 ppm H_2O (35). McCubbin et al. (36) consider possible analytical reasons for the hydrogen deficiency of kaersutite in the Chassigny meteorite and find higher values, yielding preeruptive water and mantle source estimates of 0.8–1.5 wt% and 130–250 ppm, respectively. Thus, significant discrepancies and open questions exist as to whether martian meteorite parent magmas contained appreciable water, and by inference, the state of hydration of the martian mantle.

Enough water to form a global layer on the order of approximately 400 m thick is required to explain features formed by water on the surface of Mars (37). Although the higher water contents obtained from Chassigny (36) come closer to providing this amount of water, it is unclear whether mantle water contents derived from martian meteorites are representative for the whole martian mantle. Chassigny is approximately 1.3 Ga, and most shergottites are less than 600 Ma (2), and thus their preeruptive water contents may not be applicable to Noachian degassing. However, the shergottites tap ancient mantle reservoirs. Enrichment in water of the more oxidized, incompatible element enriched mantle endmember is a predicted consequence of crystallization of a magma ocean, assuming water acts as an incompatible element (25). Intriguingly, those shergottites with Li trends in pyroxene that suggest magmatic degassing are the same that may be derived from a more oxidized, incompatible element enriched mantle reservoir.

Recent results of Mars exploration cast further doubt as to whether the geologic evolution of Mars inferred from the meteorites can be applied to Mars as a whole. As an example, superchondritic CaO/Al_2O_3 ratios in the shergottites are best explained by majoritic garnet fractionation in a deep magma ocean (38, 39). In contrast, Mars Exploration Rovers (MER) results (40) show that the approximately 3.7 Ga Gusev basalts have chondritic CaO/Al_2O_3 ratios, and are Al-enriched and derived from mantle sources more enriched in K relative to shergottites, indicating that Gusev basalts and shergottites are derived from different mantle sources (40, 41). The trend of increasing redox state with long-term incompatible element enrichment holds for the majority of the shergottites, with few exceptions. A significant question is whether the same trend holds for nonmeteoritic martian basalts. Recent estimates of oxygen fugacity for the Gusev basalts show a range of values similar to shergottites; correlation between fO_2 and K content is indicated, a trend not observed in the shergottites. Explanations for the differences between shergottite and Gusev basalt mantle sources include regional magma "seas" of differing depths, or mantle plumes, as opposed to a global magma ocean. These differing scenarios have very different implications for the mantle as a source for outgassed water. Thus, the picture of Mars from the combination of data from missions and meteorites is changing. Experimental and geochemical considerations based on Martian meteorites have resulted in constraints on the composition and interior structure of Mars (38, 42). The depth of the Martian magma ocean based on siderophile element partitioning (43) and Sm and Lu isotopic constraints (44) is approximately 1,350 km. This depth has implications for the composition of primitive martian crust, and whether a deep, primitive mantle reservoir exists (45). The mantle overturn that would occur as a consequence of magma ocean crystallization has implications for the thermal state of the early core and the early core dynamo. Geophysical data from orbiting missions to Mars will place further constraints on models of interior structure and thermal state, with implications for bulk composition, mantle mineralogy, and the nature of the core (46). Ultimately, a geophysical network may be required to elucidate the details of the martian interior and provide context for the mantle sources inferred from the samples. The lucky find of a mantle xenolith—currently unrepresented in the martian meteorite suite—would provide a direct sample of the martian mantle, would place constraints on Mars' mantle mineralogy, water content and interior structure, and would complement future geophysical investigations of the martian interior. Without direct measurements or sampling of the interior, our understanding of the evolution of Mars will remain limited.

Our limited knowledge of the interior of Mars owes in part to a singular event that brought a new purpose to a floundering Mars research and exploration program. With Mars Pathfinder en route, the focus shifted from a frozen, dormant, volcanic planet to a potentially hydrologically active planet that may, at some point, have harbored life. This shift in emphasis resulted from the recognition of the carbonate-bearing, orthopyroxenite Allan Hills (ALH) 84001 (Fig. 3) as martian in 1994 (32) and subsequent suggestion in 1996 that it harbored evidence of ancient microbial life. This suggestion engaged and captured the public attention about planetary science in a way not seen since Apollo. Fifteen years later, carbonates, sulfates, water-ice, and other water-borne deposits have been discovered on the planet's surface, redefining the hydrologic and geologic history of Mars.

Allan Hills 84001, initially classified as a diogenite, was recognized as martian during a comprehensive study of diogenites (47). Like diogenites, it is an orthopyroxene cumulate, but the most remarkable difference was the discovery of carbonate assemblages (rosettes with Ca-rich cores surrounded by alternating Mg- and Fe-rich rims) among the mostly orthopyroxenitic cumulate minerals (47). The carbonates, mainly found in fracture zones within the rock, are suggestive of formation from a fluid. Interest in ALH 84001 grew upon the discovery that it is by far the oldest sample of the martian crust in our collections. ALH 84001 is ancient (4.51 ± 0.11 Ga , preferred age based on Rb–Sr and Sm–Nd according to ref. 2), although its status as a possible sample of the primitive martian crust is in doubt as a result of the more recent Lu–Hf age of 4.09 ± 0.03 Ga (48) and its relatively unusual composition as an orthopyroxene cumulate. The ancient age of ALH 84001 suggests that it may have survived the postulated warm, wet period that formed valley networks on Mars and the presence of fluid-deposited carbonates made this meteorite a particularly inviting target for study.

Carbonates inherently contain information about the environmental conditions under which they formed. The discovery of carbonates in ALH 84001 ultimately led us to the search for life on that planet. It also sparked intense debate around the conditions of carbonate formation and whether life could have even formed under those conditions. Inferred mechanisms and temperatures of formation ranged from low temperature ($<150\,°C$) precipitates (49–51) or evaporites amenable to life (52, 53), to inferred high-temperatures (700 °C), based on equilibrium phase relationships of carbonates, prohibitive to life (54, 55). A later shock history overprints the carbonate formation with evidence for multiple impact events (47, 56, 57) and shock pressures of 49–60 GPa and temperatures exceeding 600 °C.

In 1996, McKay et al. (58) presented several lines of evidence that, taken collectively, they asserted were evidence for ancient microbial life on Mars. These lines of evidence included the presence of these indigenous martian carbonate minerals similar to some terrestrial biogenic carbonate; the formation of this carbonate in the presence of water; ovoid to elongate forms potentially sampling fossilized nanobacteria; magnetite, pyrrhotite and greigite grains within the carbonates possibly formed as waste products by magnetotactic bacteria; and the presence of polycyclic aromatic hydrocarbons (PAHs) that may have formed by the decomposition of these bacteria. The assertion of past life, some points of which still generate persistent debate 15 y later, has been largely discounted by the scientific community. A variety of alternative scenarios, including nonbiogenic precipitation of carbonates (59), followed by thermal decomposition to at least 470 °C during shock to form magnetites and PAHs (60), have gained wider acceptance in explaining the origins of the various features in ALH 84001. Whereas generally negated, the impact that this one study had on the future of Mars science, and planetary science in general, was unprecedented.

The last 15 y of Mars science (indeed, most planetary science) has centered on the search for ancient or extant life elsewhere in the Solar System. Rather than focus directly on the search for ancient or extant life, which is difficult within the confines of current space-borne technology and challenging in interpreting evidence for fossil microbial life that may date back billions of years, effort has been directed toward finding ancient or extant environments amenable to life. Terrestrial analogs of carbonates similar to those found in ALH 84001 were studied from Svalbard and extreme environments including Antarctica, the acidic Rio Tinto, the hot springs of Yellowstone, deserts such as the Atacama, and isolated saline lakes like Mono Lake (61–65) were all searched to understand the extremes for microbial life. Whereas geomicrobiology had gained a solid foundation prior to 1996, few terrestrial studies were undertaken as analogs in searching for and understanding the possibilities of life elsewhere in the Solar System.

In addition to reinvigorating laboratory studies of meteorites and analog studies of extreme environments, the suggestion of ancient life in ALH 84001 revitalized the Mars Exploration Program, launching a flotilla of new missions to Mars. Despite unexpected failures of the Mars Polar Lander and Mars Climate Orbiter, the success of the orbital Mars Odyssey, Mars Reconnaissance Orbiter, and the European Space Agency's Mars Express and landed Mars Exploration Rovers (MER) Spirit and Opportunity and the Phoenix mission have revolutionized our understanding of early Mars.

Nowhere is this more evident than in our newfound understanding of the history of water on Mars. Prompted by the suggestion of water-formed hematite from the thermal emission spectrometer on Mars Odyssey, the MER rover Opportunity discovered abundant hematite and sulfates in Meridiani Planum, suggestive of deposition by acidic fluids (66). Whereas fluids of high acidity and salinity can support microbial life on Earth, it is less clear that life could have evolved initially in such fluids. In contrast to these acidic fluids, the observation of spectral signatures from the OMEGA instrument aboard Mars Express indicate abundant phyllosilicates in the Noachian terrains of Mars (67). This finding suggests that the earliest history of ars was dominated by more neutral fluids capable of supporting life. These phyllosilicate deposits are the likely target for the Mars Science Laboratory and, dependent on the findings, the Mars Astrobiology Explorer-Cacher, which would be the first of three Flagship-class missions needed in a plan to return samples to Earth (68).

At the same time that these missions have focused on past climatic history of Mars, another set of missions are focused on volatiles currently in the subsurface and atmosphere of Mars. The Phoenix mission uncovered solid ice in the subsurface of Mars (69) whereas the planned Mars Atmostphere and Volatile Evolution Mission and joint National Aeronautics and Space Administration (NASA)-European Space Agency Mars Trace Gas Orbiter will explore the planet's upper atmosphere, ionosphere, and interactions with the sun and solar wind and search for traces of methane suggested by ground-based observations, respectively. With clear evidence for atmosphere-surface-subsurface coupling within the martian system, a clearer understanding of the history and habitability of the planet is dependent on understanding the complex interactions between these reservoirs.

Mars sample return remains the highest priority in Mars exploration. The likely target is aqueously altered or deposited rocks from the Noachian terrains of Mars, which could elucidate atmosphere-hydrosphere-crust interactions during the history of the planet.. However, Mars has had a complex history and placing those interactions in a time sequence is essential to deciphering this history. Thus, laboratory dating of a returned sample from an outcrop of a laterally extensive terrain, particularly one that marks an important relative-age boundary (e.g., Hesperian–Noachian) could place much of Mars geologic history in an absolute age reference frame, thereby allowing direct comparisons between meteorite laboratory studies and spacecraft studies. Yet even these studies only satisfy a portion of understanding the interactions between the atmosphere, hydrosphere, crust and interior of the planet. An igneous sample from a Noachian terrain, especially one likely part of the primitive martian crust, would contribute significantly to the understanding of the early geologic evolution of Mars. Mars needs its own "Genesis Rock," like 15415 from the Moon. Understanding the interior would be further enhanced by recovery of a suite of minimally shocked basaltic samples that could be analyzed for radiogenic isotopes; major, minor, and trace elements; and fO_2 to test whether the mantle of Mars contains more than the few reservoirs suggested by the shergottites and nakhlites, and elucidate the timing of differentiation of any previously unrecognized mantle reservoirs. Finally, Mars sample return offers the opportunity to directly sample the atmosphere of Mars, further elucidating its chemistry. Together, this range of samples—perhaps achievable by a single sample return mission—would promise dramatic advances in our understanding of Mars as a whole.

1. Clayton RN, Mayeda TK (1996) Oxygen isotope studies of achondrites. *Geochim Cosmochim Acta* 60:1999–2017.
2. Nyquist LE, et al. (2001) Ages and geologic histories of Martian meteorites. *Space Sci Rev* 96:105–164.
3. McSween HY, Stolper EM (1980) Basaltic meteorites. *Sci Am* 242:54–63.
4. Bogard DD, Johnson P (1983) Martian gases in an antarctic meteorite. *Science* 221:651–654.
5. Zipfel J, et al. (2011) Bounce Rock—A shergottite-like basalt encountered at Meridiani Planum, Mars. *Meteorit Planet Sci* 46:1–20.
6. Marvin UB (1983) The discovery and initial characterization of Allan-Hills-81005—the 1st Lunar Meteorite. *Geophys Res Lett* 10:775–778.
7. Vickery AM, Melosh HJ (1987) The large crater origin of SNC meteorites. *Science* 237:738–743.
8. Nyquist LE (1983) Do oblique impacts produce martian meteorites? *Proceedings of the 13th Lunar and Planetary Science Conference* (American Geophysical Union, Washington, DC), pp A785–A798.
9. Head JN, Melosh HJ, Ivanov BA (2002) Martian meteorite launch: High-speed ejecta from small craters. *Science* 298:1752–1756.
10. Hamilton VE, Christensen PR, McSween HY, Bandfield JL (2003) Searching for the source regions of martian meteorites using MGS TES: Integrating martian meteorites into the global distribution of igneous materials on Mars. *Meteorit Planet Sci* 38:871–885.
11. Lang NP, Tornabene LL, McSween HY, Christensen PR (2009) Tharsis-sourced relatively dust-free lavas and their possible relationship to Martian meteorites. *J Volcanol Geotherm Res* 185:103–115.
12. Jones JH (1986) A discussion of isotopic systematics and mineral zoning in the shergottites: Evidence for a 180 m.y. igneous crystallization age. *Geochim Cosmochim Acta* 50:969–977.
13. Borg LE, Nyquist LE, Taylor LA, Wiesmann H, Shih CY (1997) Constraints on Martian differentiation processes from Rb–Sr and Sm–Nd isotopic analyses of the basaltic shergottite QUE 94201. *Geochim Cosmochim Acta* 61:4915–4931.
14. Fritz J, Artemieva N, Greshake A (2005) Ejection of Martian meteorites. *Meteorit Planet Sci* 40:1393–1411.
15. Borg LE, Nyquist LE, Wiesmann H, Shih C-Y, Reese Y (2003) The age of Dar al Gani 476 and the differentiation history of the martian meteorites inferred from their radiogenic isotopic systematics. *Geochim Cosmochim Acta* 67:3519–3536.
16. McSween HY, Taylor GJ, Wyatt MB (2009) Elemental composition of the Martian crust. *Science* 324:736–739.
17. Bouvier A, Blichert-Toft J, Vervoort JD, Gillet P, Albarede F (2008) The case for old basaltic shergottites. *Earth Planet Sc Lett* 266:105–124.
18. Symes SJK, Borg LE, Shearer CK, Irving AJ (2008) The age of the martian meteorite Northwest Africa 1195 and the differentiation history of the shergottites. *Geochim Cosmochim Acta* 72:1696–1710.
19. Walton EL, Kelley SP, Herd CDK (2008) Isotopic and petrographic evidence for young Martian basalts. *Geochim Cosmochim Acta* 72:5819–5837.
20. Papike JJ, Karner JM, Shearer CK, Burger PV (2009) Silicate mineralogy of martian meteorites. *Geochim Cosmochim Acta* 73:7443–7485.
21. Blinova A, Herd CDK (2009) Experimental study of polybaric REE partitioning between olivine, pyroxene and melt of the Yamato 980459 composition: Insights into the petrogenesis of depleted shergottites. *Geochim Cosmochim Acta* 73:3471–3492.

22. Borg LE, Draper DS (2003) A petrogenetic model for the origin and compositional variation of the martian basaltic meteorites. *Meteorit Planet Sci* 38:1713–1731.
23. Wadhwa M (2001) Redox state of Mars' upper mantle and crust from Eu anomalies in shergottite pyroxenes. *Science* 291:1527–1530.
24. Herd CDK, Borg LE, Jones JH, Papike JJ (2002) Oxygen fugacity and geochemical variations in the martian basalts: Implications for martian basalt petrogenesis and the oxidation state of the upper mantle of Mars. *Geochim Cosmochim Acta* 66: 2025–2036.
25. Herd CDK (2003) The oxygen fugacity of olivine-phyric martian basalts and the components within the mantle and crust of Mars. *Meteorit Planet Sci* 38:1793–1805.
26. Carr MH, Head JW (2010) Geologic history of Mars. *Earth Planet Sc Lett* 294: 185–203.
27. Leshin LA, Epstein S, Stolper EM (1996) Hydrogen isotope geochemistry of SNC meteorites. *Geochim Cosmochim Acta* 60:2635–2650.
28. Dann JC, Holzheid AH, Grove TL, McSween HY, Jr (2001) Phase equilibria of the Shergotty meteorite: Constraints on pre-eruptive water contents of martian magmas and fractional crystallization under hydrous conditions. *Meteorit Planet Sci* 36:793–806.
29. Jones JH (2007) The edge of wetness: The case for dry magmatism on Mars, II. *Workshop on Water in Planetary Basalts* (abstr).
30. McSween HY, et al. (2001) Geochemical evidence for magmatic water within Mars from pyroxenes in the Shergotty meteorite. *Nature* 409:487–490.
31. Herd CDK, Treiman AH, McKay GA, Shearer CK (2005) Light lithophile elements in martian basalts: Evaluating the evidence for magmatic water degassing. *Geochim Cosmochim Acta* 69:2431–2440.
32. McSween HY, Harvey RP (1993) Outgassed water on Mars—Constraints from melt inclusions in SNC meteorites. *Science* 259:1890–1892.
33. Watson LL, Hutcheon ID, Epstein S, Stolper EM (1994) Water on Mars—Clues from deuterium/hydrogen and water contents of hydrous phases in Snc meteorites. *Science* 265:86–90.
34. Filiberto J, Treiman AH (2009) Martian magmas contained abundant chlorine, but little water. *Geology* 37:1087–1090.
35. Mysen BO, Virgo D, Popp RK, Bertka CM (1998) The role of H_2O in Martian magmatic systems. *Am Mineral* 83:942–946.
36. McCubbin FM, et al. (2010) Hydrous magmatism on Mars: A source of water for the surface and subsurface during the Amazonian. *Earth Planet Sc Lett* 292:132–138.
37. Carr MH (1996) *Water on Mars* (Oxford University Press, New York) p 229.
38. Bertka CM, Fei YW (1997) Mineralogy of the Martian interior up to core-mantle boundary pressures. *J Geophys Res-Sol Ea* 102:5251–5264.
39. Bertka CM, Holloway JR (1994) Anhydrous partial melting of an iron-rich mantle. 2. Primary melt compositions at 15 Kbar. *Contrib Mineral Petr* 115:323–338.
40. McSween HY, et al. (2004) Basaltic rocks analyzed by the Spirit rover in Gusev Crater. *Science* 305:842–845.
41. Schmidt ME, McCoy TJ (2010) The evolution of a heterogeneous Martian mantle: Clues from K, P, Ti, Cr, and Ni variations in Gusev basalts and shergottite meteorites. *Earth Planet Sc Lett* 296:67–77.
42. Dreibus G, Wanke H (1985) Mars, a volatile-rich planet. *Meteoritics* 20:367–381.
43. Righter K, Chabot NL (2011) Moderately and slightly siderophile element constraints on the depth and extent of melting in early Mars. *Meteorit Planet Sci* 46:157–176.
44. Debaille V, Yin QZ, Brandon AD, Jacobsen B (2008) Martian mantle mineralogy investigated by the Lu-176-Hf-176 and Sm-147-Nd-143 systematics of shergottites. *Earth Planet Sc Lett* 269:186–199.
45. Elkins-Tanton LT, Hess PC, Parmentier EM (2005) Possible formation of ancient crust on Mars through magma ocean processes. *J Geophys Res-Planet* 110:E12S01.
46. Khan A, Connolly JAD (2008) Constraining the composition and thermal state of Mars from inversion of geophysical data. *J Geophys Res-Planet* 113.
47. Mittlefehldt DW (1994) ALH84001, a cumulate orthopyroxenite member of the Martian meteorite clan. *Meteoritics* 29:214–221.
48. Lapen TJ, et al. (2010) A younger age for ALH84001 and its geochemical link to shergottite sources in Mars. *Science* 328:347–351.
49. Romanek CS, et al. (1994) Record of fluid–rock interactions on Mars from the meteorite Alh84001. *Nature* 372:655–657.
50. Treiman AH (1995) A petrographic history of Martian meteorite ALH84001—2 shocks and an ancient age. *Meteoritics* 30:294–302.
51. Valley JW, et al. (1997) Low-temperature carbonate concretions in the Martian meteorite ALH84001: Evidence from stable isotopes and mineralogy. *Science* 275:1633–1638.
52. McSween HY, Harvey RP (1998) An evaporation model for formation of carbonates in the ALH84001 Martian meteorite. *Int Geol Rev* 40:774–783.
53. Warren PH (1998) Petrologic evidence for low-temperature, possible flood-evaporitic origin of carbonates in the Allan Hills 84001 meteorite. *Meteorit Planet Sci* 33: A162–A163.
54. Harvey RP, McSween HY (1996) A possible high-temperature origin for the carbonates in the Martian meteorite ALH84001. *Nature* 382:49–51.
55. Bradley JP, McSween HY, Harvey RP (1998) Epitaxial growth of nanophase magnetite in Martian meteorite Allan Hills 84001: Implications for biogenic mineralization. *Meteorit Planet Sci* 33:765–773.
56. Treiman AH (1998) The history of Allan Hills 84001 revised: Multiple shock events. *Meteorit Planet Sci* 33:753–764.
57. Corrigan CM, Harvey RP (2004) Multi-generational carbonate assemblages in martian meteorite Allan Hills 84001: Implications for nucleation, growth, and alteration. *Meteorit Planet Sci* 39:17–30.
58. McKay DS, et al. (1996) Search for past life on Mars: Possible relic biogenic activity in Martian meteorite ALH84001. *Science* 273:924–930.
59. Golden DC, et al. (2000) An experimental study on kinetically-driven precipitation of calcium-magnesium-iron carbonates from solution: Implications for the low-temperature formation of carbonates in martian meteorite Allan Hills 84001. *Meteorit Planet Sci* 35:457–465.
60. Zolotov MY, Shock EL (2000) An abiotic origin for hydrocarbons in the Allan Hills 84001 martian meteorite through cooling of magmatic and impact-generated gases. *Meteorit Planet Sci* 35:629–638.
61. Aguilera A, et al. (2007) Distribution and seasonal variability in the benthic eukaryotic community of Rio Tinto (SW, Spain), an acidic, high metal extreme environment. *Syst Appl Microbiol* 30:531–546.
62. Reysenbach AL, et al. (2006) A ubiquitous thermoacidophilic archaeon from deep-sea hydrothermal vents. *Nature* 442:444–447.
63. Priscu JC, et al. (1999) Geomicrobiology of subglacial ice above Lake Vostok, Antarctica. *Science* 286:2141–2144.
64. Navarro-Gonzalez R, et al. (2003) Mars-like soils in the Atacama Desert, Chile, and the dry limit of microbial life. *Science* 302:1018–1021.
65. Wolfe-Simon F, et al. (2010) A bacterium that can grow by using arsenic instead of phosphorus. *Science*, DOI:10.1126/science.1197258.
66. Squyres SW, et al. (2004) In situ evidence for an ancient aqueous environment at Meridiani Planum, Mars. *Science* 306:1709–1714.
67. Bibring JP, et al. (2005) Mars surface diversity as revealed by the OMEGA/Mars Express observations. *Science* 307:1576–1581.
68. Squyres SW, et al. (2011) *Vision and Voyages for Planetary Science in the Decade 2013–2022* (National Academy Press, Washington, DC).
69. Renno NO, et al. (2009) Possible physical and thermodynamical evidence for liquid water at the Phoenix landing site. *J Geophys Res-Planet* 114:E00E03.