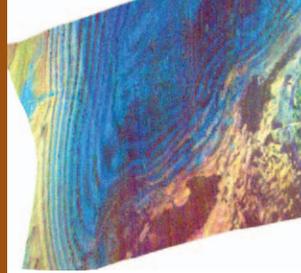


Sulfur on Mars

Penelope L. King^{1,2} and Scott M. McLennan³

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False color IR image of a mound from Juventae Chasma, Mars, with polyhydrated sulfates (blue), szomolnokite (yellow), and kieserite (orange) (Bishop et al. 2009).

The sulfur cycle is arguably the most important geochemical cycle on Mars because the transfer of sulfur places limits on Mars's differentiation processes, sedimentary, geomorphic and aqueous processes, past climate, and current and past habitability. The presence of sulfur-rich compositions on Mars is suggested by meteorite data, in situ bulk chemical and mineralogical analyses, remote sensing data from dust and surfaces, and geochemical models. The inferred sulfur-rich nature of Mars may have resulted in an Fe–(Ni)–S core that has been liquid throughout Mars's history. On the surface, Mg- and Ca-sulfates are widespread and Fe³⁺-sulfates are found locally. It is likely that these minerals occur in a variety of hydration states and host much of the mineral-bound hydrogen in the Martian subsurface.

KEYWORDS: Martian meteorites, Martian surface, sulfides, sulfates, Mars's sulfur cycle, planetary exploration

INTRODUCTION

Sulfur is central to studies of Mars's planetary-scale processes, surface evolution, climate history, and potential habitable environments. Mars has long been considered a "sulfur-rich planet." Data from Martian meteorites suggest elevated sulfur concentrations in the interior, and Martian surface deposits contain high levels of sulfur (SO₃ up to ~37 wt%, average ~6 wt%), probably in the form of sulfate salts. These salts provide clues to unique Martian hydrologic and sulfur (S) cycles that we are just beginning to unravel. In this contribution, we highlight key mineralogical and geochemical evidence from Martian meteorites and Mars's surface that provides insight into the S cycle on Mars.

SULFUR IN MARTIAN METEORITES

Primary Phases

Four meteorites that were observed to fall, and collected soon after (Shergotty, Zagami, Nakhla, and Chassigny), are widely accepted to come from Mars and are interpreted as being minimally affected by terrestrial processes (Leshin and Vicenzi 2006). In addition to these rare falls, ~50 additional meteorites of Martian parentage have been found, mainly in Antarctica and the northern African deserts. These "Martian" meteorites have up to ~0.2 wt%

S (Meyer 2008), and this S content has been used as an upper limit for the S content of Mars's mantle and core (see below). Most primary igneous S is concentrated in sulfides (<1%), including pyrrhotite, rare chalcopyrite and/or cubanite, pentlandite, troilite–pentlandite–chalcopyrite intergrowths, pyrite (likely hydrothermal), and some secondary marcasite (references in Meyer 2008). Most sulfides are located near rims of pyroxene (Fig. 1) or in interstitial mesostasis, indicating that the late-stage magmatic liquids were rich in S.

Because sulfides are located near grain boundaries and are readily weathered, they are very susceptible to alteration by fluids (even at low fluid/rock ratios) and readily form S-bearing secondary phases. To date, Mössbauer spectrometers deployed by the Mars rovers Spirit and Opportunity have not detected Fe-sulfides in any igneous (or sedimentary) rocks or soils.

Sulfur-Bearing Secondary Phases

Sulfur is found in a variety of secondary phases in Martian meteorites: sulfates, impact glasses, iddingsite, and carbonates. Sulfates are especially labile due to their high solubility and the sensitivity of phase transitions to relative humidity and temperature; therefore, it is necessary to document textural features, age, and isotope signatures, which can provide evidence in support of a Martian origin

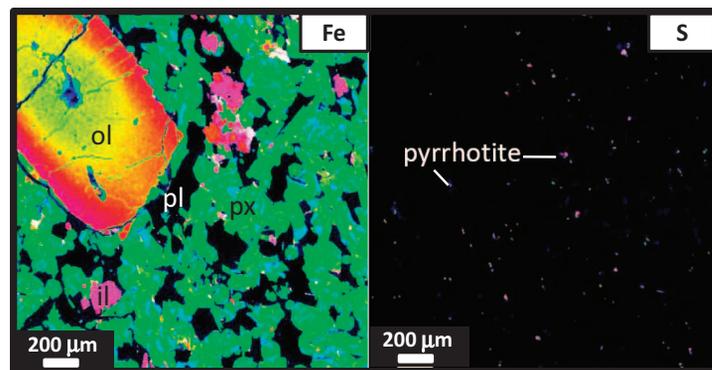


FIGURE 1 Iron and sulfur distribution in the Martian meteorite NWA1110, where ol = olivine, pl = plagioclase, px = pyroxene, and il = ilmenite. UNPUBLISHED X-RAY MAPS COURTESY OF PAUL BURGER AND JIM PAPIKE, UNIVERSITY OF NEW MEXICO

1 Institute of Meteoritics, The University of New Mexico Albuquerque, NM 87131, USA
E-mail: penking@unm.edu

2 Department of Earth Sciences, The University of Western Ontario London, ON N6A 5B7, Canada

3 Department of Geosciences, State University of New York at Stony Brook, Stony Brook, NY 11794-2100, USA
E-mail: scott.mclennan@sunysb.edu

(e.g. Leshin and Vicenzi 2006). Ca- and Mg-sulfates have been observed in the interiors of some Martian meteorites (i.e. inside fusion crusts), suggesting that these secondary minerals formed on Mars (e.g. Bridges et al. 2001; Ming et al. 2008). Iron-bearing sulfates (some with Na, K, or P) have been identified in Martian meteorites, but only a jarosite $[\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6]$ trapped in a melt inclusion (McCubbin et al. 2009) likely formed on Mars. Na-sulfates in some meteorites found in Antarctica likely represent terrestrial contamination.

The Martian meteorite EETA79001 (an Antarctic find) contains gas-rich impact-melt glasses with substantial S contents ($\text{SO}_3 < 22 \text{ wt}\%$). The S contents are interpreted to be derived from secondary sulfates on the Martian surface that were incorporated into the impact melt (Rao et al. 2008). The Shergotty glasses have $\text{SO}_3 < \sim 3 \text{ wt}\%$, but some contain Ca-sulfate crystals (Rao et al. 2008). Finally, S was reported in iddingsite ($< 0.69 \text{ wt}\% \text{SO}_3$) and carbonate ($< 0.26 \text{ wt}\% \text{SO}_3$) (Rao et al. 2008).

Sulfur Isotopes

Mass-independent S-isotope anomalies in both sulfides and sulfates have been identified in Martian meteorites (summarized in Farquhar et al. 2007). A key finding is that secondary sulfides (> 3.5 billion years old, Ga) from the ancient ALH84001 meteorite and sulfates from the 1.3 Ga Nakhla meteorite contain negative ^{33}S mass-independent anomalies ($\Delta^{33}\text{S} = -0.5$ to -1.25‰). In both cases these anomalies were interpreted to be indigenous to Mars and, if so, most likely resulted from photochemical reactions in the ancient Martian atmosphere. Accordingly, these data provide compelling evidence that a surficial S cycle has operated on Mars for at least 3.5 billion years. In the case of the Nakhla sulfides, the S isotope data also suggest a component of hydrothermally derived S.

SULFUR AND SULFATES ON THE MARTIAN SURFACE

Bulk Sulfur Chemistry

Almost forty years ago, X-ray fluorescence analyses from the Viking missions revealed that Mars has S- and Cl-rich surface regoliths or “soils” (Clark et al. 1976). No S-speciation data were collected, but the red color of the soils suggested

that S^{6+} likely predominates and that the S is hosted in sulfates. Sulfate salts were identified using telescope-based spectroscopy of Martian dust, and sulfates were proposed by various authors using geochemical models. Subsequent landed missions confirmed high S contents using APXS instruments: either an alpha-*proton* X-ray spectrometer (Pathfinder mission) or an alpha-*particle* X-ray spectrometer (Mars Exploration Rover, MER, mission). Native S has not been identified on Mars thus far.

Dust, ubiquitous on Mars’s surface and in its atmosphere, has an average SO_3 content of 6.8 wt% (2.7 wt% S), and soils have an average SO_3 content of $\sim 6.2 \text{ wt}\%$ (2.5 wt% S) (Taylor and McLennan 2009). These values are higher than the average S content of the top few tens of centimeters of the global Martian surface ($\text{SO}_3 = 4.4 \text{ wt}\%$), mapped using the Gamma Ray Spectrometer (GRS) on the 2001 Mars Odyssey spacecraft (Fig. 2; McLennan et al. 2010). The lower average S value determined by the GRS, compared to average soils, constrains the relative distributions of soil and igneous bedrock exposed at the surface. Overall, these findings are consistent with the suggestion that S has been extensively transported and deposited across the Martian surface.

Remobilization of S on Mars is also supported by a strong correlation between the degree of alteration and the SO_3 content of Martian rock surfaces and the amount of dust and soil. The lowest SO_3 contents ($\sim 1.1 \text{ wt}\%$) were found on basaltic rocks where the surface was cleaned with a Rock Abrasion Tool (RAT). However, it is possible that even those surfaces contained some S-rich debris or dust or had been altered by S-bearing fluids. Some extensively altered rocks in the Columbia Hills (Gusev Crater) have SO_3 contents that are higher in the rock interior than on the surface, suggesting that the rock interior is cemented by sulfates. To date, the highest SO_3 values measured on Mars were obtained on white-yellow soil exposed in Spirit rover’s wheel ruts and inferred to be comprised of Fe^{3+} -sulfates (e.g. the Arad site, $\text{SO}_3 = 35.1 \text{ wt}\%$; Fig. 3A).

Sulfate Mineralogy from the Mars Exploration Rovers

Sulfate mineralogy was inferred during the MER mission by correlating APXS-derived SO_3 and major cation contents (accounting for silicates and oxides), Mössbauer spectroscopy, visible and near-infrared (VNIR, PANCAM) spectra

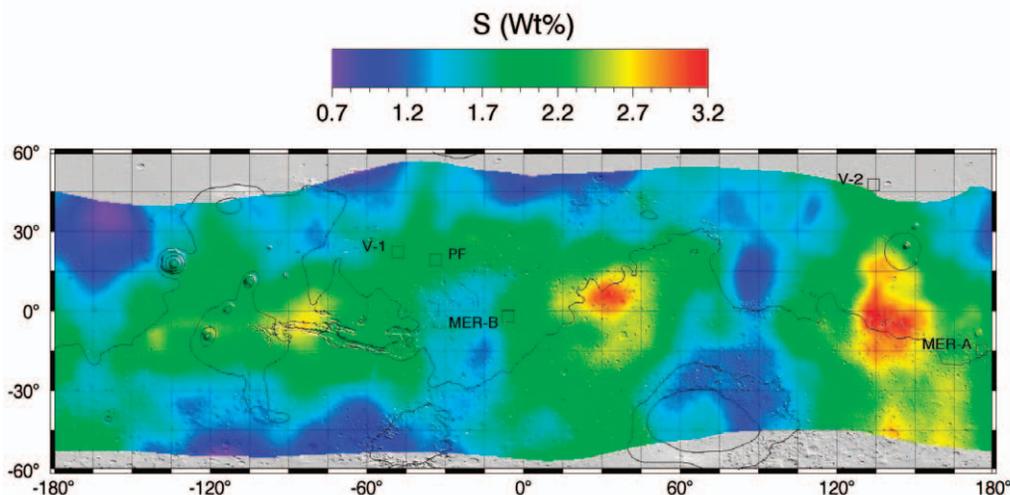


FIGURE 2 Sulfur concentration in the upper few decimeters of the Martian surface, as mapped by the Mars Odyssey Gamma Ray Spectrometer. The map is based on $10^\circ \times 10^\circ$ bins using a boxcar filter with a smoothing radius of 25° and is draped onto a Mars Orbiter Laser Altimeter shaded-relief map. Regions of

very high hydrogen content are not shown (grey) due to the presence of abundant subsurface ice. Viking (V-1, V-2), Pathfinder (PF), Spirit (MER-A), and Opportunity (MER-B) landing sites are also plotted. FROM MCLENNAN ET AL. (2010)

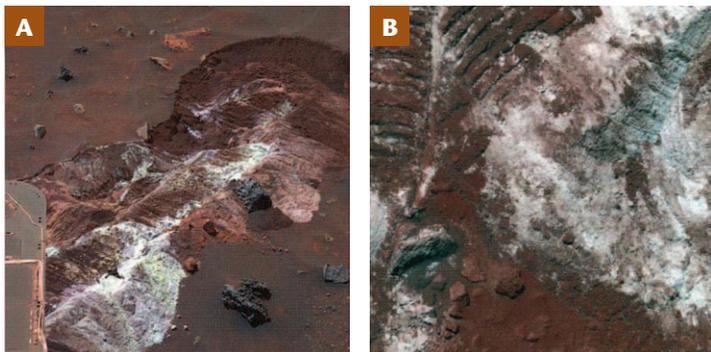


FIGURE 3 False-color PANCAM images of (A) the Arad soil (trench is 30 cm across) and (B) Paso Robles soils (40 cm across). Both are inferred to contain hydrous Fe^{3+} -sulfates, as well as Mg- and Ca-sulfates. SOURCE NASA/JPL/CORNELL

and/or thermal emission infrared (mini-TES) spectra. Below, we highlight two important sulfate localities investigated during the mission.

Meridiani Planum The rover Opportunity discovered S-rich outcrops, informally termed the Burns formation, soon after landing on the Meridiani plains (see review in McLennan and Grotzinger 2008). These outcrops consist of a sequence of “wetting upwards” eolian sandstones, in which repeated episodes of groundwater recharge periodically breached the surface to form local, subaqueous depositional settings. Sulfates are interpreted to represent a suite of evaporative minerals and their diagenetic products. The SO_3 contents of these sedimentary rocks are high (18 to 25 wt%). The Mössbauer spectrometer identified about 10% jarosite—an important line of evidence for low-pH aqueous conditions during deposition. Based on geochemistry and thermal infrared spectroscopy, other sulfate minerals are inferred to consist of a mixture of ~18% Mg-sulfate and ~10% Ca-sulfate of unknown hydration states, and possibly Na-bearing sulfates (Clark et al. 2005; McLennan and Grotzinger 2008).

Paso Robles Soils, Columbia Hills, Gusev Crater S-rich soils termed “Paso Robles class” (FIG. 3A, B) are widespread in Gusev Crater’s inner basin and contain Fe^{3+} -, Mg-, and Ca-sulfates. The Fe^{3+} -sulfates dominate, based on studies using Mössbauer, VNIR (with two different data-processing methods), mini-TES, and APXS spectroscopies. Ferricopiapite [$\text{Fe}^{3+}_{4.6}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$] has been identified by all methods, and other Fe-sulfates commonly proposed include coquimbite, fibroferrite, parabutlerite, and rhomboclase (e.g. Lane et al. 2008).

Sulfate Mineralogy at the Phoenix Lander Site

Evidence for sulfate phases at the Phoenix Lander site in the north polar region has been ambiguous. However, a recent reevaluation indicates that water-soluble SO_4^{2-} contents of 1.4 ± 0.5 wt% are present in the soils and that this is likely related to a Mg-sulfate phase (Kounaves et al. 2010).

Sulfate Mineralogy from Remote Observations

Sulfate minerals have been identified on the Martian near-surface using VNIR spectra collected with the Mars Express Observatoire pour la Minéralogie, l’Eau, les Glaces et l’Activité (OMEGA) and the Mars Reconnaissance Orbiter Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) instruments. OMEGA has found extensive deposits of kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) and gypsum (Gendrin et al. 2005; Bibring and Langevin 2008). These sulfates occur in the

equatorial Valles Marineris canyon system and adjacent Meridiani area (Meridiani Planum, Aram Chaos, Valles Marineris, and Terra Meridiani), and gypsum deposits are prevalent in the northern circumpolar erg deposits (e.g. Bibring and Langevin 2008) but were not observed at the Phoenix Lander site. In addition, an unidentified “polyhydrated sulfate” has been identified at several locations. Ferric oxides are commonly associated with polyhydrated sulfates and may also be associated with kieserite (Bibring and Langevin 2008).

CRISM data for Mars were recently summarized by Murchie et al. (2009), who recognized five types of sulfate deposits: (1) *Meridiani-type layered deposits* (e.g. Terra Meridiani and Aram Chaos) consist of monohydrated or polyhydrated sulfates (probably Mg rich) superposed on cratered terrain, with some layers rich in hematite. (2) *Valles-type layered deposits* (in Valles Marineris) contain polyhydrated sulfates that overlie monohydrated sulfates in discrete layers. They infill chasmata, form mounds, and form deeply eroded plateaus up to several kilometers in relief. These deposits may be deformed, and some have layers rich in ferric oxides, oxyhydroxides, or hydrated sulfates. (3) *Intracrater clay-sulfate deposits* (e.g. craters in Terra Sirenum) have hydrated sulfate layers interbedded with kaolinite layers and are exposed on crater walls. (4) *Gypsum plains* (north polar erg and layered deposits) are made of sandy material and reworked into dunes, probably with other hydrated minerals. (5) *Siliceous layered deposits* (e.g. plains surrounding Valles Marineris) consist of jarosite associated with amorphous silica layers.

SULFUR IN MARTIAN RESERVOIRS

S in the Martian Mantle and Core

Sulfur was delivered to Mars during accretion and by later impactors (FIG. 4A). The S content of Martian meteorites has been used to argue that Mars and its mantle are intrinsically S rich and that the core is particularly S rich. There is little direct evidence for the S content of Mars’s mantle, although enrichments compared to Earth’s mantle are expected (Gaillard and Scaillet 2009; Righter et al. 2009). Higher S contents on Mars are favored by Mars’s higher mantle FeO content and the likelihood that it had a shallower magma ocean than Earth (e.g. Righter et al. 2009). A S-rich core (~10.6–16.2 wt%; Stewart et al. 2007) is suggested by limited geophysical data indicating that the core may be completely or partially molten. Melting may occur if S is added to an Fe(–Ni) core because the liquidus is lowered relative to Mars’s pressure–temperature profile (Stewart et al. 2007). If the core was liquid throughout Martian history, as implied by this hypothesis, then the thermal remanent magnetism of some Noachian southern highland rocks would be due to vigorous core convection before ~3.7 Ga. (Noachian refers to >~3.7 Ga; Hesperian ~3.7–~3.0 Ga; and Amazonian, after ~3.0 Ga. Surface ages are obtained by comparing crater counts with the lunar cratering record. Boundary ages are highly uncertain, especially for the Hesperian–Amazonian boundary.) The shutdown of such a convection system and the consequent loss of the magnetic field have important implications for models of Mars’s heat production, plate tectonics, and atmosphere and climate evolution.

S in the Martian Crust and Atmosphere

Ultimately, the indigenous S on Mars’s surface must have come from the mantle and crust (planetary and impactor leaching in FIG. 4A) in the form of magmatic or hydrothermal S-bearing gas, immiscible sulfide fluids, and/or sulfide minerals (King and McSween 2005). Righter et al. (2009) calculated that degassing of 2400 ppm S from

Fe-rich Martian melts over Mars's geologic history may have produced all the S at the surface. However, they caution that any degassing model relies on knowing whether the melt is S saturated (i.e. degasses S species) or whether sulfide saturation has been reached. Thus, to fully understand the degassing history of Martian magmas, we require additional constraints, such as the initial S content, oxygen fugacity, pressure, temperature, and composition of the magma, including the concentrations of other volatile elements, like water (see Métrich and Mandeville 2010 this issue). Nonetheless, Martian meteorites indicate that S is hosted in late-stage magmatic sulfides, and it is likely that much S was transported in fluids and gases (FIG. 4B), such as magmatic gases, acid sulfate fumaroles, hot springs, and hydrothermal fluids (as evidenced by the S isotope ratios in Nakhla sulfides). Deposits resulting from these high-temperature processes might include hydrated silica-sulfate deposits and intracrater clay-sulfate deposits (FIG. 4B).

Sulfur gases have not been detected in the current Martian atmosphere, possibly because H₂S and SO₂ form sulfate minerals readily through photochemical reactions (FIG. 4B), as suggested by Δ³³S values in Martian meteorite sulfates (Farquhar et al. 2007). However, if residence times and fluxes were such that atmospheric sulfur gases were at significant concentrations, they may have acted as an efficient greenhouse gas and warmed the Martian climate (Johnson et al. 2008). An interesting, but yet untested, suggestion is that early in Mars's history, sulfur was less efficiently oxidized during atmospheric processing, leading to the formation of sulfite minerals (Halevy et al. 2007). In any case, sulfur species were then incorporated into sedimentary and hydrological cycles on the planet's surface and near-surface (e.g. McLennan and Grotzinger 2008; Ming et al. 2008; FIG. 4B).

SULFATES IN SEDIMENTARY AND HYDROLOGIC SETTINGS ON MARS

Sulfate Brines and Sulfate Crystallization

Layered sulfate deposits (e.g. Meridiani-type and Valles-type) and the gypsum plains were probably derived through sedimentary, hydrologic, glacial, and diagenetic processes (FIG. 4B, C); specifically, the sulfates likely crystallized from brine. Intracrater clay-sulfate layered deposits and the Paso Robles soils may have formed through brine processes. The crystallization sequence and identity of the sulfate minerals on Mars depend on the initial bulk composition of brines (including the salt/water ratio) and intensive parameters such as pH, temperature, and partial pressure of oxygen (PO₂). Accordingly, there are several conceptual end member models for Martian fluids in which these parameters differ, but all such models may be relevant on Mars. Below we discuss the geochemical models in which brine compositions are derived from mafic-ultramafic rocks, because this is most relevant to the Martian surface (e.g. FIG. 4A, B).

Low-fluid/rock-ratio and low-pH models An acidic nature for the Martian surface is suggested by the abundance of S, the occurrence of jarosite and other Fe³⁺-sulfates with amorphous silica, experiments simulating the alteration of basalt under acidic conditions, and geochemical models of rover data (Tosca et al. 2005; Tosca and McLennan 2006; Hurowitz et al. 2006). Acidic weathering on Mars under low fluid/rock ratios (e.g. FIG. 4C) would differ from typical weathering on Earth because acidic conditions promote preferential dissolution of olivine, apatite, and Fe-Ti oxides relative to pyroxene and plagioclase; slow oxidation of Fe²⁺; increased Al and Fe solubility; and the production of amorphous silica during alteration, whereas Al- and Fe³⁺-clays

and Fe³⁺-oxides are not formed (Hurowitz et al. 2006). Brines produced by acid sulfate weathering of typical Martian crust (olivine basalt) are rich in Mg, Fe²⁺, Ca, and SO₄²⁻. Tosca and McLennan (2006) modeled acidic brines using a chemical-divide approach with varying HCO₃²⁻/SO₄²⁻ ratios (i.e. initial pH) in the starting brine to generate evaporite assemblages that match those identified on Mars.

Low-pH, variable-PO₂ models Extremely acidic conditions (high H₂SO₄ molality, pH < ~2) result in Fe²⁺- and SO₄-rich solutions that are predicted to precipitate Fe²⁺-sulfates (King and McSween 2005; Tosca et al. 2005), such as szomolnokite (Fe²⁺SO₄·H₂O; Bishop et al. 2009). Under oxidizing conditions, Fe²⁺-sulfates then form mixed Fe²⁺-Fe³⁺-sulfates, followed by Fe³⁺-sulfates (like jarosite), and finally Fe³⁺-oxides/hydroxides/oxyhydroxides (hematite/ferrihydrite/goethite) which "age" to form hematite. This sequence may be obtained following a path of either dehydration → oxidization → neutralization (King and McSween 2005) or oxidization → aqueous diagenesis (Tosca et al. 2008).

Near-neutral-pH models Neutral-pH brines may be produced on Mars through melting of ice or snow in contact with rocks or dust or through neutralization of initially acidic solutions by reaction with silicate minerals. In either case, such solutions likely would be salt rich and water poor in order for salts to form on the Martian surface. Neutral- to alkaline-pH environments on Mars are suggested by the occurrence of clays and carbonates on the Martian surface (OMEGA and CRISM data) and carbonates in Martian meteorites. Weathering of Martian basalt by a near-neutral solution results in Mg-Na-Ca-SO₄-(Cl)-rich solutions, similar in bulk composition to average Martian soil. In this case, Fe³⁺-oxides/hydroxides/oxyhydroxides precipitate early with phosphates, possibly followed by carbonates (Fe-, then Ca-, then Ca-Mg-carbonates), followed in turn by Ca-sulfates, Mg(-Na)-sulfates, and finally Na-halides (King et al. 2004). If the fluid/rock ratio was higher or the interaction time longer, then Al- and Fe³⁺-clay minerals may have formed.

SULFATE AGE, PRESERVATION, AND RECYCLING ON MARS

The timing of sulfate deposition is poorly constrained but most likely occurred early in Martian history. OMEGA data were used to propose three distinct alteration periods in Mars's history: (1) early, alkaline, water-rich alteration, producing phyllosilicates (>3.7 Ga; Noachian); (2) acidic, water-rich alteration, producing sulfates (Late Noachian/Hesperian); and (3) young, anhydrous alteration, producing ferric oxides (Late Hesperian/Amazonian; Bibring et al. 2006). In this model, the acidic environment that formed the sulfates resulted from climate change, perhaps due to massive SO₂ degassing during Tharsis volcanism. Subsequent models suggested that Meridiani-type and Valles-type layered sulfate rocks formed in the Late Noachian to Early Hesperian (~3.5 Ga) as a result of large-scale groundwater recharge during the Tharsis volcanic episode (Andrews-Hanna et al. 2007; Murchie et al. 2009; FIG. 4B). Other sulfate deposit types likely formed through a range of processes (e.g. high-temperature processes or precipitation from a range of brine compositions under a variety of conditions) throughout Martian history and over a range of distances. Future orbital and rover data may allow quantitative tests of models of sulfate formation (for example, using mineral abundances and mass balance coupled with detailed stratigraphy).

Sulfate remobilization and redeposition on Mars likely occurred episodically over time (for example, as observed at Meridiani Planum). These events may have been in

FIGURE 4 Schematic S cycle on Mars at (A) the planetary scale, (B) the crustal scale, and (C) the small scale (based on King et al. 2004; Murchie et al. 2009). Some possible deposit types are given in italics.

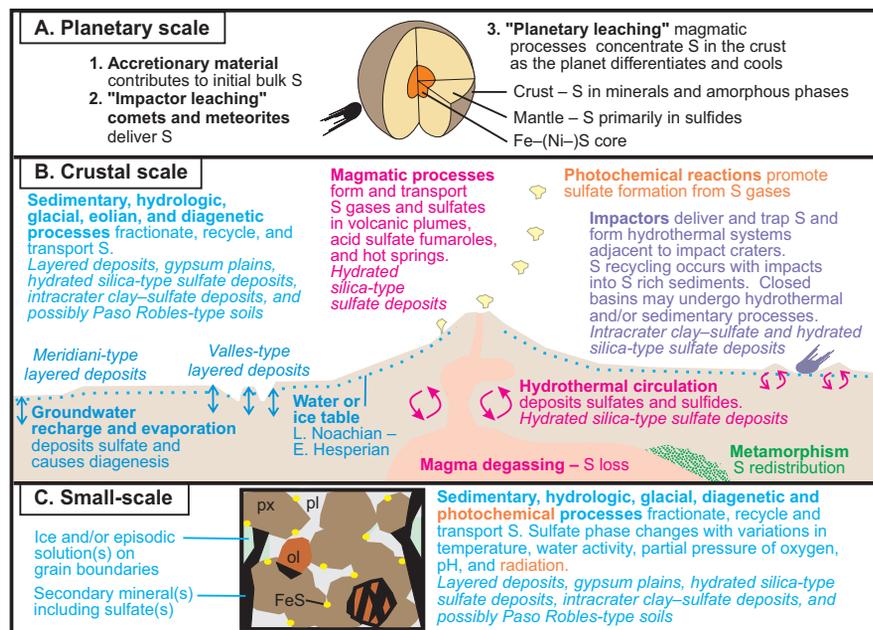
response to aqueous alteration triggered by volcanic, hydrothermal, or impact events; eolian activity; outflow channels and mass flow; seasonal sublimation and dehydration events; obliquity cycles; diagenesis and thermal maturation; and the formation of solution films on mineral surfaces (FIG. 4B, C) (King et al. 2004; McLennan and Grotzinger 2008). Remobilization events may have played a role in changing the pH of solutions on Mars's surface: rhomboclase [$\text{HFe}^{3+}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$] produces acid when it breaks down, whereas jarosite consumes acid and commonly produces Fe^{3+} -oxides.

The preservation of large amounts of sulfates on Mars's surface relative to Earth's highlights some major differences in the two planets' geologic histories and environments. Sulfate deposition requires water-limited conditions (low water activity or relative humidity, $a_{\text{H}_2\text{O}}$) because many of these minerals are very soluble. Sulfates are probably preserved on Mars because any surface solutions have largely been lost and only existed episodically on the surface, and because relatively low temperatures (at least since ~3.7 Ga) favored their preservation (King et al. 2004). Lack of plate tectonics caused S to be concentrated near the surface as it would have been derived from volcanic and fluid-rock reactions. On Earth, on the other hand, S is recycled in subduction zones and redistributed during formation and chemical fractionation of continental crust as well as in the hydrologic cycle (weathering, river input, etc.; King et al. 2004; McLennan and Grotzinger 2008). Finally, on Mars, there are no documented mechanisms for reducing sulfate, in contrast to Earth where mid-ocean-ridge hydrothermal brines deposit sulfides and biological activity commonly reduces sulfate (King et al. 2004).

SULFATE HYDRATION STATE(S) ON MARS

Mg-, Ca-, and Fe-sulfates may contain H as OH^- or H_2O or both, with total H_2O contents up to ~60%. Accordingly, sulfates may host the majority of mineral-bound H on Mars. The hydration state in sulfates is controlled by $a_{\text{H}_2\text{O}}$ and temperature and is influenced by the overall chemistry of the system (e.g. Vaniman and Chipera 2006). In the case of Mg-sulfate minerals, hydration states vary from ~1 (kieserite and a pseudomorph), through 2, 4, 6, and 7, to 11 (meridianiite), with other hydrated phases also recognized (Wang et al. 2009). Fe-sulfate assemblages are also sensitive indicators of the PO_2 , pH, and bulk composition (e.g. King and McSween 2005), and studies defining Fe-sulfate phase relationships are underway in several laboratories.

Current diurnal variations of both relative humidity and temperature on Mars are such that multiple hydration states should be stable at or near the surface, although uncertain kinetic factors will also influence such reactions. In situ techniques have not identified mineral hydration states with any confidence (Ming et al. 2008). Remote sensing data collected over more than two Mars years showed no detectible variation in the hydration state of kieserite deposits overlain by polyhydrated sulfates (Roach



et al. 2009). The geologic history of adjacent sulfate deposits with differing hydration states is enigmatic and may only be explained by multiple events (e.g. precipitation, diagenesis and thermal maturation, dehydration, aqueous alteration; Roach et al. 2009). Climate change associated with past variations in the planet's obliquity has likely played a role in the formation and long-term stability of near-surface hydrated sulfates.

Dehydration of sulfate minerals is accompanied by large molar volume changes; for example, when meridianiite dehydrates to form epsomite at 2°C, there is a 34% loss of the solid volume (Peterson and Wang 2006). Volume changes associated with sulfate dehydration-rehydration processes have been suggested as a possible explanation for a variety of geomorphic and textural features on Mars, including some catastrophic outflow features and gullies, secondary pores and veins in sedimentary rocks, physical properties of the soils (e.g. clods), and the formation of small-scale fracture and vein systems (e.g. FIG. 4C).

SUMMARY: THE SULFUR CYCLE ON MARS

The sulfur cycle dominates many geologic processes on Mars. Substantial amounts of S were delivered to Mars in accretionary materials and through later impactors (FIG. 4A), resulting in a S-rich planet. Sulfur partitioned into the core to form a liquid Fe-(Ni)-S core, which may have undergone a period of rapid convection during the Noachian, causing a transient magnetic field. Transfer of S to the crust through degassing, magmatism, and hydrothermal processes resulted in substantial S at the surface (FIG. 4A, B). Photochemical reactions of S gases likely resulted in rapid sulfate formation and may have warmed the early Martian climate. Sedimentary and hydrologic processes dominated the surface S cycle, including S fractionation, recycling, and transport (FIG. 4B, C). Several plausible models exist for sulfate-brine formation and crystallization, and it is likely that multiple sedimentary and hydrologic events have affected sulfate assemblages. Impactors may have played a role in delivering and trapping S (e.g. in melts); impact events may have caused near-surface hydrothermal systems capable of transporting S phases and recycling S from sulfate-rich deposits (FIG. 4B). In summary, the Martian sulfur cycle is central to past and present aqueous, atmospheric, sedimentary, and geomorphic processes on Mars.

FUTURE DIRECTIONS

The upcoming Mars Science Laboratory mission will provide unparalleled information on the S mineralogy and geochemistry of the Martian surface. The environment of sulfate formation may be determined, provided we have appropriate phase equilibria and reaction-kinetic models, and sufficient information to infer the geologic setting. Understanding Martian sulfate mineralogy and textural relations will make it possible to assess the past and current habitability of Mars and the likelihood of biomarker pres-

ervation. Samples returned from Mars in the future would greatly expand our understanding of the Martian sulfur cycle.

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