GEOCHEMISTRY OF SEDIMENTARY PROCESSES ON MARS

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Abstract: Mars has an extensive, long-lived sedimentary record that is complimentary to the terrestrial record, bearing both first-order similarities and first-order differences. The igneous record is composed of basaltic rocks, in fundamental contrast to the granodioritic upper continental crust of the Earth, which in turn dominates the provenance of clastic and chemical sedimentary rocks. The crust and sedimentary mass of Mars on average are older than the terrestrial records, and Mars provides exceptional potential for understanding processes that were active during the earliest history (>3.5 Gyr) of the solar system. Numerous sedimentary minerals have been identified both from orbit and by rovers/landers and include a variety of clays, sulfates, amorphous silica, minor carbonates, and possibly chlorides. The Martian sedimentary mineralogical record is Fe- and Mg-enriched and Na- and K-depleted compared to the terrestrial record, reflecting differing crustal compositions and differing aqueous surficial environments. There is evidence for three distinct sedimentary mineralogical epochs: an early clay-rich era, intermediate sulfate-rich era, and a younger era dominated by secondary iron oxides. This mineralogical evolution likely records desiccation, acidification, and oxidation of the surface over geological time. There is also evidence that surficial processes were controlled by a sulfur cycle, rather than the carbon cycle, over much of Martian geological time, leading to low-pH aqueous conditions. The nature of this S cycle changed over time as volcanic sulfur sources and amounts of near-surface water diminished. There is a linkage between the S cycle and iron/oxygen cycles related to diagenetic oxidation of iron sulfates to form iron oxides. Where studied in detail, weathering is dominated by low pH, with mobility of ferric iron being common. Lack of evidence for expected aluminum mobility indicates that low water–rock ratio conditions prevailed. In Noachian terrains, where clay minerals are common, it is more likely that aqueous conditions were closer to circum-neutral, but detailed study awaits future landed missions. Numerous depositional environments are recognized, including fluvial, deltaic, lacustrine, eolian, and glacial settings. Evaporitic rocks appear common and are characterized by distinctive suites of Mg-, Ca-, and Fe-sulfates and possibly chlorides. A system of chemical divides can be constructed and indicates that the range of observed evaporite minerals can be explained by typical water compositions derived from acidic weathering of Martian crust, and with variable initial pH controlled by HCO_3^-/SO_4^{2-} ratios. Several diagenetic processes have also been identified, including complex groundwater diagenetic histories. One process, consistent with experimental studies, that explains the correlation between sulfate and iron oxide minerals seen from orbit, as well as formation of hematitic concretions in the Burns Formation on Meridiani Planum, is oxidation of iron sulfates to form iron oxides. In general, the diagenetic record that has been identified, including incomplete iron sulfate oxidation, limited clay mineral transformations, and absence of amorphous silica recrystallization, indicates highly water-limited postdepositional conditions. Among the most important outstanding questions for sedimentary geochemistry are those related to the quantification of the size and lithological distribution of the sedimentary record, the detailed history of near-surface water, and the origin and history of acidity in the aqueous environment.

Key words: Mars, geochemistry, sedimentary rocks, weathering

INTRODUCTION

The first decade of the 21st century has witnessed what must be described as a revolution in our understanding of the geology of Mars. During this time, there have been no fewer than four spacecraft orbiting the planet (Mars Surveyor, Mars Odyssey, Mars Express, Mars Reconnaissance Orbiter) and three more exploring its surface (*Spirit, Opportunity, Phoenix*), each returning large volumes of mostly complementary geological, geophysical, geochemical, and mineralogical data. With committed international engagement and launch opportunities approximately every 26 months, continued exploration of the Martian stratigraphic record including, in due course, the return to Earth of Martian sedimentary samples, appears reasonably assured (e.g., Pratt et al. 2010). Recent reviews of the general geology and geochemistry of Mars can be found in Nimmo and Tanaka (2005), Carr (2006), Soderblom and Bell (2008), Taylor and McLennan (2009), Carr and Head (2010), Grotzinger et al. (2011), Fassett and Head (2011), and McSween and McLennan (2012).

Among the many discoveries that have been made is the growing recognition of a very long-lived, highly dynamic sedimentary rock cycle that has both first-order similarities and first-order differences with regard to the terrestrial record (McLennan and Grotzinger 2008). Indeed, a well-preserved sedimentary record on Mars can be traced back into the Early Noachian era, over 4.0 billion years ago. Eolian and glacial processes are ongoing at the Martian surface today, and, accordingly, the preserved stratigraphic record of Mars very likely represents a longer interval of geological time than that recorded in the stratigraphic record of the Earth (Fig. 1). Most of the crust of Mars—and thus a large fraction of the preserved Martian sedimentary record—is very ancient (>3 Gyr), and for those interested in comparative planetology, this record is highly complementary to the stratigraphic record of Earth, which is mostly young, and indeed holds promise for providing a higher-resolution record of the early history of the solar system than may ever be available in the terrestrial record.

Although sedimentary geologists have found much that is very familiar, as described elsewhere in this volume, there are also important first-order differences between the geological and stratigraphic records of the two planets (e.g., McLennan and Grotzinger 2008, Taylor and McLennan 2009, Grotzinger et al. 2011). For example, there is little evidence that plate tectonics were ever active on Mars, and, accordingly, the development and evolution of sedimentary basins proceeded within a very different tectonic regime. The great antiquity of much of the stratigraphic record means that impact processes must have played a dominant role in the formation and distribution of sedimentary particles (e.g., Barnhart and Nimmo 2011) and in the development of sedimentary basins. Mars is a "basaltic planet" with no evidence for significant exposures of evolved granitic crust, so characteristic of the terrestrial upper continental crust, and thus the chemical and mineralogical composition of the primary sources of both clastic and chemical sediment differ fundamentally. Because of the low gravity and atmospheric pressure on Mars, volcanic processes also differ (Wilson and Head 1994, Carr 2006), one effect being that despite

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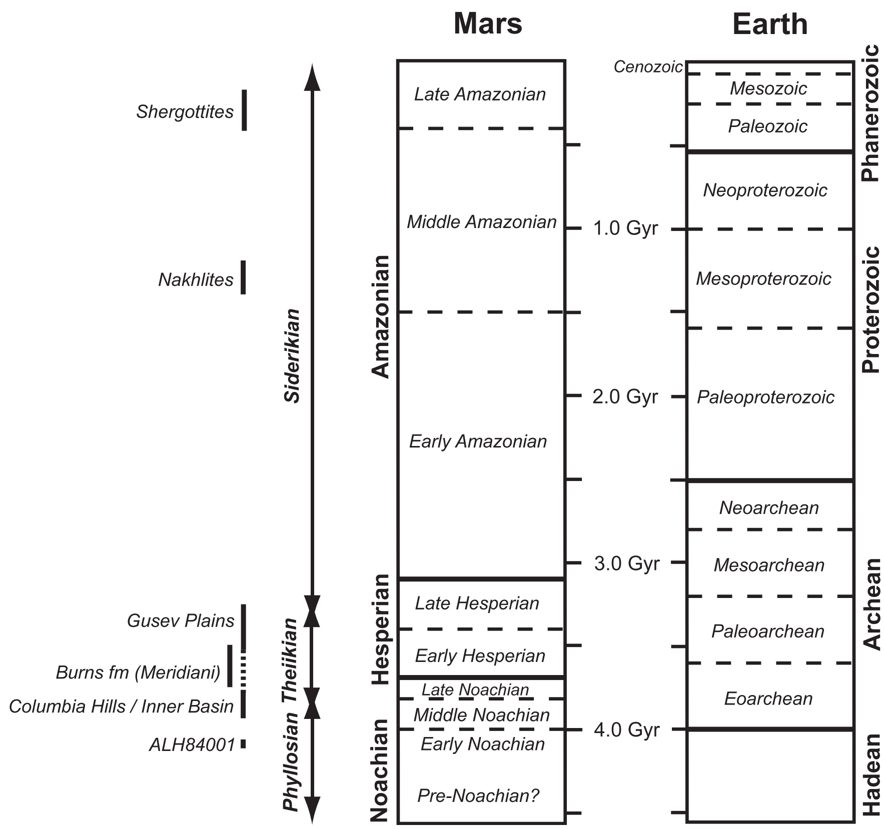

FIG. 1.—Comparison of the geological timescales for Mars and Earth. Also shown are the approximate ages of the mineralogical epochs defined by Bibring et al. (2006), sedimentary rocks studied by the rovers *Spirit* (Gusev Plains, Columbia Hills, Inner Basin) and *Opportunity* (Meridiani), and the radiometric ages of the different Martian meteorites. The overall preserved stratigraphic record for Mars dates from present-day sedimentological activity into the Early Noachian, equivalent to the terrestrial Hadean Eon, which has no preserved sedimentary record. Note that the absolute ages of Martian chronostratigraphic boundaries, taken from Head et al. (2001) and Hartmann (2005), are highly uncertain and are especially so for younger periods.

basaltic igneous compositions, pyroclastic deposits should be more common on Mars than on Earth. Finally, there is evidence that some version of a sulfur cycle, rather than a carbon cycle, may have dominated surficial processes on Mars during significant parts of its geological history, resulting in very different aqueous conditions that influenced weathering, sedimentation, and diagenesis.

McLennan and Grotzinger (2008) reviewed many of the constraints on our current understanding of the physical and chemical processes involved with the Martian sedimentary rock cycle. However, even since then new insights and some growing consensus have been forthcoming (e.g., Grotzinger et al. 2011). For example, we have a better understanding of the diversity and bulk composition of the upper crust that acts as the ultimate source of sediment (McSween et al. 2009, Taylor and McLennan 2009). Recognition of the importance of clay mineralogy, especially in the Early to Middle Noachian, and identification of long–sought-after carbonate minerals are very recent. Finally, there is a growing appreciation that some version of a sulfur cycle may at times have dominated Martian surficial processes, analogous to the way the carbon cycle dominates terrestrial processes. Accordingly, this article attempts to review a geochemical perspective of the Martian sedimentary rock cycle, focusing on recent advances in our understanding of sedimentary geochemistry/mineralogy, including the possible role that the sulfur cycle may play in governing surficial processes and thus the Martian stratigraphic record.

COMPOSITION AND EVOLUTION OF THE MARTIAN CRUST

On the Earth, the relatively evolved magmatic rocks of the upper continental crust and their metamorphic and sedimentary descendants dominate the ultimate provenance of both terrigenous and chemical components of sedimentary rocks. The composition and evolution of the upper crust is thus a critical factor in determining the chemical and mineralogical nature of the sedimentary record (Taylor and McLennan 1985), and so this is an appropriate place to begin.

The terrestrial upper continental crust is dominated by granitic rocks (sensu lato) and their extrusive and metamorphic equivalents and on average approximates to the igneous rock type granodiorite (Taylor and McLennan 1985). This crust is thus silica-rich, with elevated levels of incompatible elements (e.g., K, Th, U, and REE) and relatively low levels of ferro-magnesian elements (e.g., Fe, Mg, Cr, and Ni). This chemistry results in an average igneous mineralogy dominated by quartz, plagioclase, K-feldspar, and micas (Nesbitt and Young 1984). In contrast, basaltic rocks of mainly subalkaline to mildly alkaline affinity and their intrusive equivalents appear to dominate the Martian crust (Taylor et al. 2008, McSween et al. 2009). Estimates of bulk composition, based on orbital gamma ray chemical mapping of the Martian surface (e.g., Boynton et al. 2007) and surficial soil and dust compositions, indicate that the average Martian crust has a mildly incompatible element-enriched basalt composition (Taylor and McLennan 2009). Such a composition is likely to result in an average mineralogy dominated by plagioclase, olivine, pyroxene, and Fe-Ti oxides. Table 1 compares selected chemical and mineralogical estimates for the Martian upper crust and terrestrial upper continental crust, and Figure 2 illustrates these differences in terms of total alkali elements vs. silica.

Planetary crusts in general can be divided into the following three fundamental types based on their ultimate origin (Taylor 1989; Taylor and McLennan 2009):

1. "Primary" crusts that form as a result of initial planetary differentiation, typically through magma ocean processes, the lunar highland crust being the type example. Any primary crust that may have formed on the Earth has been lost as a result of various recycling processes. On Mars, primary crust likely exists but is profoundly disrupted by later impact processes and substantially covered by younger magmatism and sediments.

2. "Secondary" crusts that form over longer periods of time by partial melting of the mantle, the Earth's basaltic oceanic crust and lunar maria being the best-understood examples. Although secondary crusts are invariably basaltic in composition, in detail the nature of secondary crusts is highly variable throughout the solar system. Mars has a long history of magmatism, and a significant fraction of the surface is likely covered by secondary crust.

TABLE 1.—Chemical and mineralogical comparison of the upper Martian igneous crust and terrestrial upper continental crust (adapted from Nesbitt and Young [1984], McLennan and Grotzinger [2008], and Taylor and McLennan [2009]).[1]

	Mars crust	Earth upper crust
SiO_2	49.3	65.9
TiO_2	0.98	0.65
Al_2O_3	10.5	15.2
FeO_T	18.2	4.52
MnO	0.36	0.08
MgO	9.06	2.21
CaO	6.92	4.20
Na_2O	2.97	3.90
K_2O	0.45	3.36
P_2O_5	0.90	0.16
Sum	99.6	100.2
Cr	2600	83
Ni	337	44
Zn	320	71
Ba	55	550
Rb	12.5	112
La	5.5	30
Ce	13.9	64
Y	18	22
Th	0.70	10.7
U	0.18	2.8
Olivine	17	0
Pyroxene	22	1
Fe-Ti oxides	10	1
Glass	21	13
Plagioclase	29	35
K-feldspar	0	11
Sheet silicates	0	14
Quartz	0	20
Other	0	4

[1] Major elements and minerals in weight percent; trace elements in parts per million. Total iron as FeO_T.

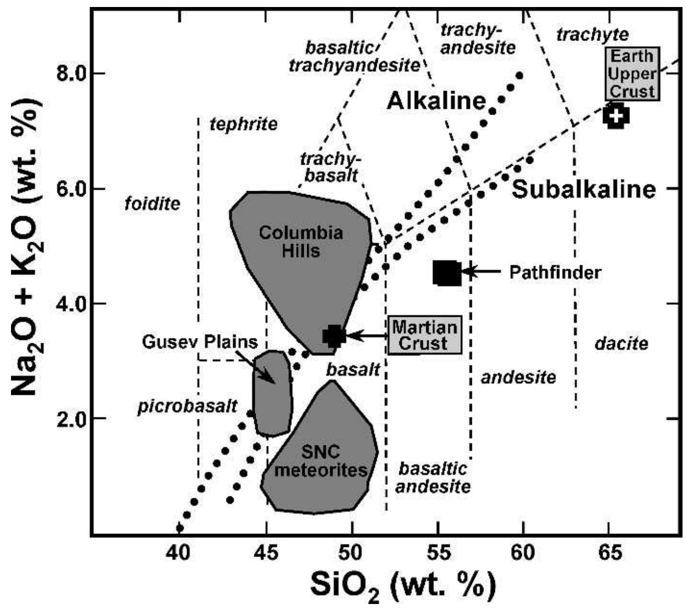

FIG. 2.—Plot of (Na_2O+K_2O) vs. SiO_2 for igneous rocks from Mars, including fields for Martian meteorites and rock samples analyzed at the Pathfinder and Spirit landing sites superimposed onto a classification scheme for volcanic rocks. Heavy dotted line shows two estimates of the boundary between alkaline and subalkaline compositions. The two large crosses are estimates of the bulk composition of the Martian upper crust and composition for the Earth's upper continental crust. The Martian crust is basaltic and has a chemical and mineralogical character that fundamentally differs from the "granodioritic" terrestrial upper crust. Adapted from Taylor and McLennan (2009) and McSween et al. (2009).

3. "Tertiary" crusts that form because of dehydration or partial melting of secondary crusts. The terrestrial continental crust is the only known example in the solar system, formed as a result of plate tectonic cycling through the mantle of the oceanic crust. The continental crust is further differentiated, predominantly by intra-crustal melting, into a more granitic upper crust (the ultimate source of most sediment) and a more mafic lower crust. Growth of continental crust has proceeded in an episodic fashion since the earliest Archean and has a mean age of about 2.5 Gyr (Taylor and McLennan 1985).

A variety of both long-lived ($^{238,235}U$-$^{206,207}Pb$, ^{187}Re-^{187}Os, ^{176}Lu-^{176}Hf, ^{147}Sm-^{143}Nd, ^{87}Rb-^{87}Sr) and short-lived (^{182}Hf-^{182}W, ^{146}Sm-^{142}Nd, ^{129}I-^{129}Xe) radiogenic isotopes indicates that Mars differentiated very early (~4.5 Gyr) into core, mantle, and primary crust, most likely as a result of magma ocean processes (e.g., Halliday et al. 2001, Elkins-Tanton et al. 2005). The oldest known example of Martian crust is the meteorite ALH84001, recently dated by Lu-Hf methods at 4.09 ± 0.03 Gyr (Lapen et al. 2010), significantly younger than previously thought (earlier estimates indicated an age of ~4.5 Gyr). Isotopic systematics are consistent with derivation from a mantle source, with characteristics similar to much younger Martian meteorites (shergottites), and so this rock is likely an example of ancient secondary crust. Crater counting techniques provide evidence that magmatic activity has continued throughout Martian history, essentially through to the present, but at drastically reduced rates over geological time (Werner 2009, Carr and Head 2010). Accordingly, the crust of Mars is mostly very ancient and dominated by a combination of old mafic primary crust and later (but still mostly old) secondary basaltic crust. Taylor and McLennan (2009) estimated that most of the Martian crust was primary, although likely highly disrupted by intense early impact bombardment (e.g., Frey 2006), with about 20 ± 10% being secondary crust. The mean age of the Martian crust then is >4.0 Gyr and much older on average than terrestrial crust. A comparison of models for the growth history of the Martian crust and terrestrial continental and oceanic crusts is provided in Figure 3.

The ages of the crusts of Earth and Mars in turn influence the age distribution of their respective sedimentary masses. The cumulative stratigraphic age distribution of the terrestrial sedimentary mass is plotted in Figure 3 (Veizer and Jansen 1985). The much younger age of the sedimentary mass compared to the continental crust has long been recognized as being related mainly to various intracrustal and sedimentary recycling processes (e.g., Garrels and Mackenzie 1971; Veizer and Jansen 1979, 1985; McLennan 1988; Veizer and Mackenzie 2003). The age distribution of the Martian sedimentary mass is very poorly constrained, not in the least as a result of the dearth of measured stratigraphic sections. Tanaka et al. (1988) quantified the surface ages (based on crater counting statistics) of different geological terrain types using Viking-era maps, and the cumulative area curve for sedimentary terrains is also shown in Figure 3. These data pre-date the recognition of abundant sedimentary rocks on Mars, which are mostly Early Hesperian and older (Malin and Edgett 2000). In addition, the regolith is likely significantly thicker in ancient terrains than in younger ones (e.g., Hartmann and Barlow 2006). Accordingly, the cumulative curve shown in Figure 3 likely represents an overall minimum age limit for the Martian sedimentary mass as a whole. Nevertheless, it is clear that the Martian sedimentary record is very ancient and on average probably less dominated by cannibalistic sedimentary recycling processes, compared to the terrestrial record, especially after about the Noachian–Hesperian boundary.

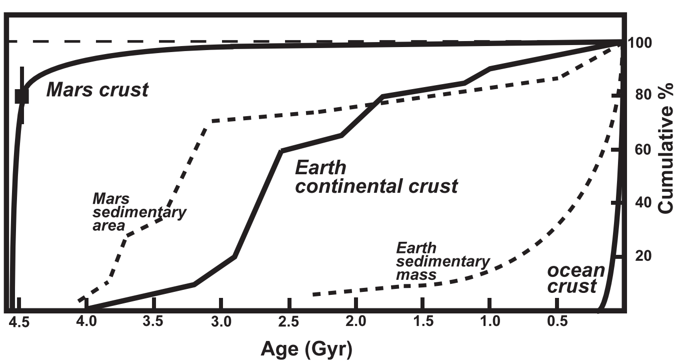

FIG. 3.—Comparison of crustal growth histories for Mars and Earth (adapted from Taylor and McLennan 2009). Also shown are cumulative growth histories for the terrestrial sedimentary mass (Veizer and Jansen 1985) and areas dominated by sedimentary deposits on Mars (Tanaka et al. 1988). The square symbol and vertical bar reflect the conclusion that 20 ± 10% of the Martian crust is secondary and formed after the crystallization of the primary crust, during solidification of an early magma ocean. The Martian crust and sedimentary mass are substantially older than Earth's continental crust and sediment. See text for further discussion.

THE SEDIMENTARY RECORD: GEOCHEMISTRY AND MINERALOGY

The present-day surface of Mars is characterized by a vanishingly thin atmosphere averaging about 6 millibars and composed mainly of CO_2, global surface temperatures averaging about −60° C and only rarely rising above 0° C, and gravitational acceleration (*g*) that is 0.38 times that of Earth. Although seasonally dynamic H_2O–CO_2 ice caps exist at both poles, conditions permitting liquid water at or near the surface only rarely exist. Nevertheless, the surface of Mars has long been recognized as having been sculpted by sedimentary processes that, in addition to the expected pyroclastic, volcaniclastic, and impact deposits, include eolian, glacial, and subaqueous activity, the latter in the form of erosional channels, branching valley networks, gullies, and lakes (see recent reviews by Carr [2006] and Carr and Head [2010]). This apparent contradiction is generally explained by proposals that Mars once had a more substantial atmosphere and more clement surface conditions, resulting from an early greenhouse effect. This early atmosphere was lost either by meteorite impact and solar wind erosion (Mars has not had a protective magnetic field since about the Early–Mid-Noachian) and/or by sequestration of CO_2 into a subsurface carbonate mineral reservoir of either sedimentary and/or hydrothermal origins. Another factor may be that in the absence of a large moon (Mars' two moons, Diemos and Phobos, measure ~12 km and ~22 km, respectively), obliquity changes are far more dramatic than on Earth, with Mars currently being in a period of exceptionally cold conditions.

Although most subaqueous activity is thought to be ancient (Noachian to Early Hesperian), there is evidence that some large channels may have formed as recently as ~100 Myr, and there is time-lapse photographic evidence for rare gully formation today (e.g., Malin and Edgett 2006). Suggestions that Mars once had an extensive ocean-sized body of water in the northern hemisphere lowlands, based primarily on geomorphological evidence, continue to appear (e.g., Di Achille and Hynek 2010) but have yet to achieve widespread consensus.

Recognition that ancient layered deposits include true lithified sedimentary rocks is recent (Malin and Edgett 2000). High-resolution spectral imaging from the Mars Express and Mars Reconnaissance Orbiter spacecrafts has revealed extensive successions of indurated layered deposits, often with complex stratal geometries, within the walls of the large canyons (e.g., Valles Marineris) and within craters in the ancient southern highlands. Layered deposits may have formed by impact, pyroclastic, volcaniclastic, and eolian processes, but recognition of a variety of secondary sedimentary minerals, including clays, sulfates, Fe-oxides, and minor carbonates, also points to a role for aqueous processes (e.g., weathering, chemical sedimentation). In some craters (e.g., Eberswalde, Holden) there is strong geomorphological and stratigraphic evidence for fans, subaqueous deltas, terraces, and outlet channels. The physical attributes of such deposits are described elsewhere in this volume, and the reader is directed there for this discussion.

In addition to orbital observations, the rovers *Spirit* and *Opportunity* evaluated ancient sedimentary rocks and soils[1] on the surface of Mars. The chemical compositions of some selected samples are listed in Table 2. A key feature of all these analyses, in addition to the basically basaltic nature of the compositions, is the elevated levels of S and Cl. The most thoroughly studied is the Late Noachian to Early Hesperian Burns Formation exposed at Meridiani Planum. The Burns Formation consists of weakly indurated, well-sorted eolian sandstones composed of sulfate-bearing grains derived from a weathered basaltic source and

[1]The term "soils" (or "regolith") is used here in the planetary sense of being an unconsolidated surficial deposit of predominantly impact and eolian origins with no implied connotation, or indeed likelihood, of biological processes or substantial vertical in situ alteration processes necessarily being involved in their formation.

TABLE 2.—Chemical composition of selected sedimentary rocks and unconsolidated surficial sediment (soils) on Mars.[1]

	Sedimentary rocks				Unconsolidated sediments (soils)				
	Meridiani Planum average Burns Formation	Columbia Hills (Peace)	Columbia Hills (Alligator)	Home Plate (Crawford)	Pathfinder average soil	Meridiani Planum basaltic soil	Gusev Plains basaltic soil	Columbia Hills basaltic soil	Average dust-rich soil
SiO_2	37.0	37.3	41.8	46.6	42.1	46.4	46.2	46.3	45.7
TiO_2	0.78	0.45	0.53	1.11	0.87	1.02	0.86	0.87	0.97
Al_2O_3	6.16	2.24	5.49	9.98	9.5	9.46	10.1	10.3	9.53
FeO_T	15.9	20.4	18.3	15.4	21.6	18.3	16.3	15.5	17.0
Cr_2O_3	0.20	0.75	0.63	0.34	0.29	0.40	0.38	0.30	0.35
MnO	0.32	0.47	0.33	0.29	0.31	0.37	0.33	0.31	0.34
MgO	7.61	21.53	16.27	10.3	7.78	7.29	8.64	8.67	7.98
CaO	5.00	4.90	4.72	6.74	6.37	7.07	6.45	6.20	6.48
Na_2O	1.69	n.d.	1.6	3.36	2.84	2.22	2.89	3.21	2.61
K_2O	0.58	n.d	0.19	0.32	0.60	0.49	0.43	0.44	0.47
P_2O_5	1.05	0.49	0.29	1.27	0.74	0.83	0.75	0.92	0.86
SO_3	22.48	10.6	8.48	2.91	6.27	5.45	5.66	6.18	6.83
Cl	1.05	0.72	1.26	1.35	0.76	0.63	0.69	0.73	0.78
Σ	**99.8**	**99.9**	**99.9**	**100.0**	**100.0**	**99.9**	**99.7**	**99.9**	**99.9**
Cr	1350	5130	4310	2330	1980	2740	2600	2050	2395
Ni	589	774	506	297	–	445	424	466	565
Zn	448	64	205	314	–	273	264	274	384
Br	102	71	217	91	–	65	52	68	64

[1] Details: Burns Formation average of 34 analyses; Pathfinder average of 7; Meridiani basaltic soil average of 8; Gusev basaltic soil average of 15; Columbia Hills average of 9; Dust-rich soil average of 8 from Gusev Plains (4) and Meridiani Planum (4). Notes: Samples in Burns Formation average, Peace, and Alligator analyses all from abraded surfaces; Crawford from brushed surface. Crawford is from the upper part of an eolian reworked pyroclastic deposit found at Home Plate. Data sources: Burns Formation from Brückner et al. (2008) and Planetary Data System; Peace and Alligator from Gellert et al. (2006); Home Plate from Squyres et al. (2007). Unconsolidated sediments from compilations reported in Taylor and McLennan (2009).

FeO_T = total iron as FeO; – = no analysis available; n.d. = not detected.

cemented by later sulfate-dominated chemical components (Squyres et al. 2004; Grotzinger et al. 2005, 2006; McLennan et al. 2005; Metz et al. 2009). To date, more than 25 m of stratigraphic section have been measured over about 10 km of lateral distance. The sands, possibly derived from a desiccating playa lake, were deposited in a dry to wet dune–interdune setting. Syn- to early postdepositional recharge of very high–ionic strength acidic groundwater, which periodically breached the surface to form local subaqueous environments, resulted in a pervasive diagenetic overprint with formation of secondary porosity, multiple generations of cements, and hematitic concretions. The Burns Formation comprises, on an anhydrous basis, approximately 40% siliciclastic components (in decreasing abundance, poorly characterized altered igneous material, plagioclase, pyroxene, and olivine) and 60% chemical constituents (amorphous silica, Mg-sulfate, Ca-sulfate, jarosite, hematite, and possibly chlorides). The presence of jarosite $[(Na,K,H_3O)Fe_3^{3+}(SO_4)_2(OH)_6]$, which typically is stable at a pH of <4, has been cited as prime evidence for low pH conditions.

The Spirit Rover has also identified older (Noachian) sedimentary rocks in Gusev Crater on the opposite side of the planet. These deposits are less well characterized because the geology and stratigraphy are more complex, exposures are less extensive, and far less detailed work has been carried out on each exposure. Included are layered deposits that have detrital textures and have been interpreted to mostly represent pyroclastic, volcaniclastic, impact, and eolian deposits (Squyres et al. 2006). Notable examples include the rock Peace, exposed in the Columbia Hills, that appears to be a Mg-sulfate–cemented mafic–ultramafic sandstone and a cross-bedded well-sorted sandstone unit preserved above a coarse pyroclastic unit (e.g., containing a bomb sag) at a large outcrop called Home Plate. The Home Plate sandstone has essentially the same chemical composition as the underlying pyroclastics and, accordingly, is interpreted to have been deposited by eolian reworking of the underlying unit (Squyres et al. 2007, Lewis et al. 2008).

An important result of orbital remote sensing and in situ Mössbauer and visible-infrared spectroscopy coupled with chemical data is that a wide diversity of secondary sedimentary minerals exists on the surface of Mars (see recent review in Murchie et al. [2009]). Common secondary detrital constituents include a range of smectites, from Fe/Mg-rich to relatively aluminous and other phyllosilicates, including the more aluminous kaolin-group minerals, as well as mixed-layer clay minerals, illite, chlorite, and possibly prehnite. Chemical constituents that have been identified include hydrated Mg-, Ca-, and Fe-sulfates; amorphous silica; secondary iron oxides; chlorides; and Mg-carbonates. Compared to terrestrial settings, this sedimentary mineral suite tends to be Fe- and Mg-rich and Na- and K-poor, likely reflecting both the differing composition of the crustal sources and differing aqueous conditions of alteration and deposition (Table 3; see below).

Orbital spectral mapping of Martian sedimentary deposits has led to the suggestion that there may be distinctive sedimentary mineralogical epochs through Martian geological history (Bibring et al. 2006). Such an evolution perhaps should not be surprising and, although differing greatly in detail, could be analogous to the terrestrial mineralogical evolution, for which as many as 10 distinct mineralogical stages over ~4 Gyr of Earth history have been proposed (Hazen et al. 2008). For Mars, mineralogical changes are interpreted to reflect an evolution in the amount and composition of near-surface water available for surficial processes. In this model, the Martian surface has effectively

TABLE 3.—Comparison of selected common sedimentary mineralogy observed on Earth with known sedimentary mineralogy on Mars with idealized chemical formulas.[1]

Earth		Mars	
Sand-sized detrital			
Quartz	SiO_2	Plagioclase	$(Ca,Na)(Si,Al)_4O_8$
K-feldspar	$KAlSi_3O_8$	Olivine	$(Fe,Mg)_2SiO_4$
Plagioclase	$(Ca,Na)(Si,Al)_4O_8$	Pyroxene	$XY(Si,Al)_2O_6$
(Intermediate-Felsic lithics)		(Mafic lithics)	
Clays			
Kaolinite	$Al_2Si_2O_5(OH)_4$	Kaolinite	$Al_2Si_2O_5(OH)_4$
Illite	$K_{0.8}Al_{2.8}Si_{3.2}O_{10}(OH)_2$	–	
Smectite[2]		Fe-Mg-smectite[2]	
e.g., $Ca_{0.17}(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH_2)2H_2O$		e.g., $(Ca_{0.5},Na)_{0.3}Fe_2(Si,Al)_4O_{10}(OH)_2\cdot nH_2O$	
Sulfates			
Gypsum	$CaSO_4\cdot 2H_2O$	Gypsum	$CaSO_4\cdot 2H_2O$
Anhydrite	$CaSO_4$	Kieserite	$MgSO_4\cdot H_2O$
		Jarosite[3]	$(Na,K,H_3O)Fe^{3+}_3(SO_4)_2(OH)_6$
		Ferricopiapite[3]	$Fe^{3+}_{0.66}Fe^{3+}_4(SO_4)_6(OH)_2\cdot 20(H_2O)$
		"Polyhydrated sulfates"[4]	
Carbonates			
Aragonite	$CaCO_3$	Mg-carbonate	?$MgCO_3$
Calcite	$CaCO_3$	Calcite	$CaCO_3$
Dolomite	$(Mg,Ca)CO_3$		
Secondary iron oxide phases			
Hematite	Fe_2O_3	Hematite	Fe_2O_3
Goethite	$FeO\cdot OH$	Goethite	$FeO\cdot OH$
		Nanophase iron oxides	
Secondary silica phases			
Opal-A	$SiO_2\cdot nH_2O$	Amorphous silica	$SiO_2\cdot nH_2O$
Opal-CT	$SiO_2\cdot nH_2O$		
Micro-, mega-quartz	SiO_2		

[1] Idealized formulas for Martian minerals are highly uncertain.
[2] Smectite compositions in terrestrial sediments are highly variable, and this is also likely the case for Mars. Formulas given here are examples. Spectral evidence does point to most Martian smectites being Fe- and Mg-rich (e.g., nontronite, saponite).
[3] Jarosite and ferricopiapite are two examples of what is likely a significantly larger number of complex ferric sulfates.
[4] Nonspecific term commonly used by spectroscopists to include higher hydrates of Mg-sulfates ($MgSO_4\cdot nH_2O$) and other sulfate salts with multiple waters of hydration.

desiccated, acidified, and oxidized over geological history. Thus, the Martian sedimentary record has been divided into three epochs, including the following (Fig. 1):

1. Phyllosian, during the Early and Mid-Noachian, during which clay minerals are common, sulfates rare, and conditions thought to be water-rich, with near-surface waters at circum-neutral pH.

2. Theiikian, during the Late Noachian through Early Hesperian, during which hydrated sulfate minerals and low pH conditions dominate. The amount of water available for surficial processes is more controversial, with estimates ranging from water-rich (Bibring et al. 2006) to highly water-limited (e.g., Hurowitz and McLennan 2007, Tosca and Knoll 2009).

3. Siderikian, during the Late Hesperian through Amazonian, during which water-limited, low-pH, and oxidizing conditions gave rise to secondary ferric oxides dominating secondary mineralogy.

Although this model has been influential in the interpretation of Martian geological history, it has not yet achieved full consensus, and a number of aspects of the model are under vigorous investigation (Grotzinger et al. 2011). As mentioned above, detailed studies relating mineralogy to physical stratigraphy are not abundant, and the amount of water involved in surficial processes, especially during the Noachian and Early Hesperian, is controversial. The origin of acidity during the Late Noachian is also unclear, with suggestions including processes such as increased volcanic activity (e.g., Bibring et al. 2006), for which there seems to be little geological evidence (e.g., Werner 2009), and hydrolysis associated with iron oxidation (e.g., Hurowitz et al. 2010). In addition, it has been noted that an early clay-rich epoch, without a complementary reservoir of chemical constituents (e.g., carbonate, sulfate, and/or chloride salts), presents global geochemical mass balance problems (e.g., Milliken et al. 2009).

THE MARTIAN SULFUR CYCLE

Terrestrial surficial processes are dominated by the long-term and short-term carbon cycles, which give rise to the acidity required for rock weathering. These acids, including carbonic acid (H_2CO_3) and a variety of organic acids, are weak (i.e., low solubility and dissociation constants), leading to the vast majority of terrestrial aqueous environments being circum-neutral, with pH mostly in the range of 5.5 to 8.5. Carbonate minerals dominate the salts that result from the weathering and breakdown of primary igneous minerals, and a large amount of carbon is stored as organic material in sedimentary rocks (e.g., Garrels and Mackenzie 1971).

The situation on Mars appears to be different. It is widely assumed that the early secondary atmosphere of Mars was dominated by CO_2, as it was for Earth and Venus. Unlike Earth, where carbon is stored in the rock record, or Venus, where CO_2 remains in the atmosphere, the fate of the Martian CO_2 reservoir is not understood. Carbonate minerals, although identified in the geological record (e.g., Morris et al. 2010) and the polar regolith (Boynton et al. 2009), do not appear to play a dominant role in observed sedimentary mineralogy. A previously unrecognized reservoir of CO_2 ice was recently identified in the south polar cap but is only the equivalent of a few millibars of atmospheric pressure (Phillips et al. 2011). Possible explanations include loss of CO_2 to space or preservation of large amounts of unobserved carbonates at depth within the crust. The former suggestion is consistent with the loss of magnetic shielding during the Noachian, when meteorite bombardment was still intense, and the latter with the presence of secondary carbonate minerals in fractures within Martian meteorites (e.g., Bridges and Grady 1999). Of course, both processes may have been operating.

The sulfur-rich character of surface soil and dust deposits has been known since the first Viking chemical analyses (Clark et al. 1976) and has been confirmed by all subsequent landed missions (see Table 2). Orbital mapping by the Mars Odyssey spacecraft has confirmed that elevated sulfur in surficial deposits is a global feature (King and McLennan 2010, McLennan et al. 2010). There is also geochemical and cosmochemical evidence to indicate that the silicate portion of Mars is significantly enriched in S compared to the Earth (e.g., Clark and Baird 1979, Wänke and Dreibus 1994, Gaillard and Scaillet 2009, Righter et al. 2009). Coupled with evidence for extensive ancient sulfate-rich sedimentary rocks, paucity of carbonates, and evidence for widespread mobility of Fe^{3+} under oxidizing conditions, these observations have led to suggestions that a sulfur cycle, characterized by low pH conditions (~pH2–pH5), rather than the carbon cycle has dominated surficial processes on Mars throughout a significant portion of its geological history (e.g., Clark and Baird 1979, Settle 1979, Farién et al. 2004, King et al. 2004, McLennan et al. 2006, Halevy et al. 2007, Johnson et al. 2008, McLennan and Grotzinger 2008, King and McLennan 2010).

An important point to keep in mind is that a sedimentary regime dominated by the sulfur cycle does not preclude the presence of significant amounts of CO_2 in the atmosphere. Dissociation constants of both sulfurous and sulfuric acid are many orders of magnitude greater than the dissociation constants of carbonic acid (e.g., Halevy et al. 2007). Accordingly, even very low concentrations of SO_2 in the atmosphere ($<10^{-5}$ bar) can lead to acidic-pH (<4) aqueous environments within a CO_2-dominated atmosphere.

Sulfur Reservoirs on Mars

Estimates of the Martian primitive mantle sulfur concentration typically are $\geq$400 ppm, or about twice that of Earth (e.g., Gaillard and Scaillet 2009, Righter et al. 2009). The composition of the Martian basaltic crust is difficult to estimate, but meteorite data and experimental results are consistent with a value of ~2000 ppm, or about twice that of terrestrial oceanic crust and four times that of the continental crust. Can we estimate the size of the sedimentary sulfur reservoir? Measurements from orbital gamma ray mapping indicate that the S content of the upper half-meter of the planet averages about 2% (King and McLennan 2010; W. Boynton, personal communication, 2009), a value broadly consistent with analyses of soil deposits by landed spacecraft (Table 2). However, there is little understanding of the mass and distribution of these deposits in space (i.e., vertically) and time (e.g., Hartmann and Barlow 2006). Sulfate minerals have been recognized from orbit in sedimentary rocks but the concentrations are poorly constrained and the overall distributions are basically unknown. The sedimentary rocks analyzed by the Mars rovers indicate S contents that are generally high but varying by over an order of magnitude in just a few locations. Accordingly, at this stage, there appears to be no way to directly estimate the average sulfur content of the sedimentary mass.

A model dependent approach to estimating the mass of the sedimentary sulfur reservoir is to examine constraints from planetary degassing. Righter et al. (2009) and Gaillard and Scaillet (2009) each estimated the amount of S degassed from the Martian mantle over geological time, and estimates ranged from 4.5×10^{19} g to 5.4×10^{21} g, respectively, with both being considered conservative estimates. The lower value of Righter et al. (2009) adopted volcanic rates from Greeley and Schneid (1991), but if more recent estimates of Noachian volcanism are considered (e.g., McEwen et al. 1999), post-magma ocean Martian volcanism could be as much as an order of magnitude greater, and, thus, the S degassing value would also increase by about an order of magnitude, bringing these S degassing estimates into closer agreement, at about 10^{21} g.

Another approach is to assume that Mars has outgassed sulfur proportionately the same as Earth. This also seems like a conservative assumption since sulfur is an incompatible element and on average Mars has differentiated more of its other incompatible elements into the crust than has the Earth (Taylor and McLennan 2009). Canfield (2004) estimated that approximately 1.1×10^{23} g, or 11% of the S in the Earth's primitive mantle, has outgassed over geological time, although much of this has also been involved with plate tectonic recycling processes, and so the amount of S at the surface at any given time is much less. If we assume that 11% of the Martian primitive mantle S has also been outgassed and if we correct for differing primitive mantle concentrations, a value of 2.3×10^{22} g of S results. In the absence of plate tectonics, any S degassed is expected to remain in the near-surface sedimentary environment.

For scale, a Martian sulfur reservoir on the order of 10^{21} to 10^{22} g is approximately equivalent to a planetary-wide sedimentary layer, with S content equal to average soil (~6% SO_3), that is between ~200 m and 2 km thick. Another way to think of it is that this mass of sulfur would equate to a planetary-wide thickness of between ~50 and 500 m of typical hydrated sulfate minerals (e.g., mixture of gypsum, kieserite, epsomite, melanterite, jarosite, etc.). Thus, the known and reasonably inferred sedimentary record appears to readily provide a reasonable sink for this amount of sulfur.

Early Sulfur Cycle

The sulfur cycle on Mars can be divided into distinctive early and late versions (Fig. 4), with the separation between them likely corresponding to the point in time during which Martian crustal growth rates subsided, some time around the end of the Hesperian (Figs. 1, 3). The early phase of the sulfur cycle would be when sulfur was actively outgassing into the surficial environment and thus providing potential acidity for aqueous weathering processes. Most magmatic activity on Mars, the ultimate source of sulfur at the surface, took place early in Martian history (>3 Gyr), during the Noachian and Hesperian (Taylor and McLennan 2009). This was also the time when

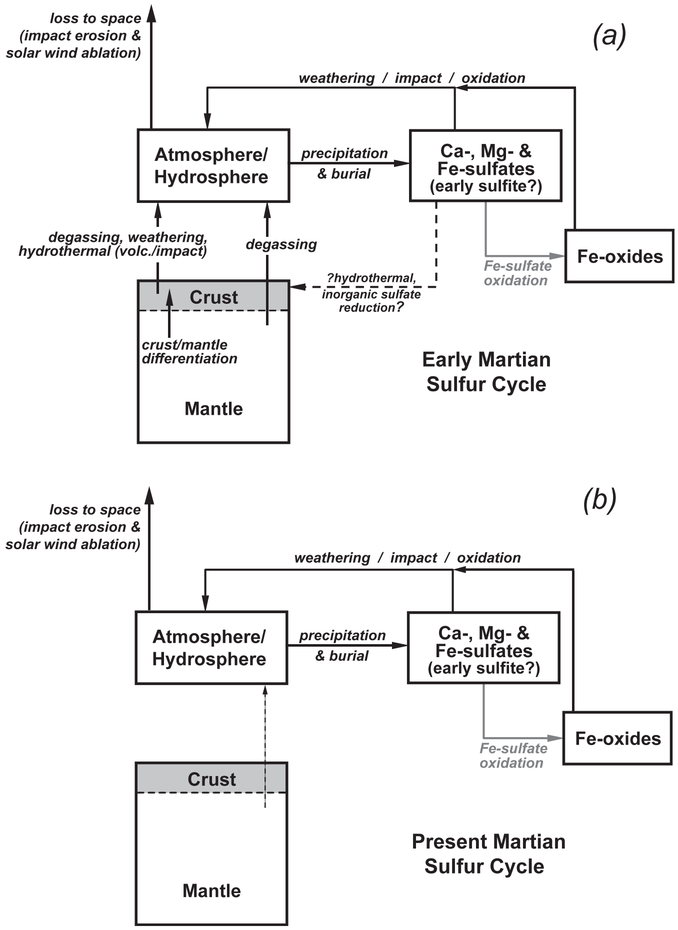

FIG. 4.—Schematic model of the sulfur cycle on Mars. (a) Possible sulfur cycle during the early history of Mars, when volcanic activity was relatively high and sulfur was delivered to the surface from mantle sources. Evidence for young volcanism, such as that represented by nakhlite and shergottite meteorites (Fig. 1), indicates that this cycle may have continued to contribute sulfur to the surface, but in a highly diminished form (Fig. 3), through later Martian history. (b) Possible sulfur cycle dominant during the youngest part of Martian geological history, when volcanic activity had substantially subsided and sulfur species taking part in surficial processes were derived mainly by recycling processes, such as impact recycling, Fe-sulfate oxidation, and sulfate weathering. Note that the sulfur cycle is linked to the iron cycle through oxidation of iron sulfates to iron oxides, shown in gray (also see Fig. 5). See text for further discussion.

relatively widespread subaqueous conditions prevailed, probably facilitated by an early greenhouse effect. Experimental and modeling studies and in situ measurements of mineralogical/chemical compositions of Martian rocks and soils can be combined to identify a variety of processes involved in the surficial S cycle (see below).

Sulfuric acid alteration of basaltic rocks and minerals is reasonably well established on the Martian surface. Processes likely included both low temperature alteration, such as that required to produce the high–ionic strength fluids responsible for evaporitic minerals at Meridiani Planum (e.g., McLennan et al. 2005, Tosca et al. 2005), and higher temperature epithermal to hydrothermal fluids, such as those responsible for a variety of mixed (including ferric) sulfates in the vicinity of Home Plate (e.g., Squyres et al. 2007, 2008). The widespread occurrence of sulfate and chloride minerals on the Martian surface observed from orbit (Murchie et al. 2009) and within rocks and soils at the landing sites points to widespread production of a variety of evaporite minerals, dominated by Ca-, Mg-, and Fe-sulfates, likely of mixed hydration state. Finally, a variety of recycling processes has been identified that have the potential for recycling sulfur through the surficial environment, including impact processes, weathering of sulfate minerals, and oxidation of ferrous and ferric sulfates to form iron oxides (see below).

One concern resulting from the low pH conditions predicted from a dominant S cycle early in Mars history is the widespread occurrence of clay and apparent dearth of sulfate minerals during the Early Noachian (e.g., Milliken et al. 2009). In order to explain this, Halevy et al. (2007) have proposed an even earlier version of a sulfur cycle. In their model, reducing conditions inhibited sulfur oxidation and, accordingly, sulfurous acid was formed from degassed SO_2 rather than being rapidly oxidized to form sulfuric acid. This scenario results in acidic but far more modest pH conditions (pH $\sim$4.5–5.5) that led to suppression of carbonate mineral precipitation but permitted formation of clay minerals. On the other hand, such a model predicts widespread formation of a variety of sulfite (i.e., $X^{2+}S^{4+}O_3$) minerals during the Early Noachian, for which there is no evidence. Indeed, it is unlikely that such minerals could survive the near-surface environment of Mars over geological time (Halevy et al. 2007).

Present-Day Sulfur Cycle

Although rates of volcanism and aqueous activity were greatly reduced after about 3 Gyr, there is evidence that surficial processes influenced by a sulfur cycle continued beyond this time. Rock surfaces analyzed by Spirit in the Gusev Crater show clear evidence of acid alteration on the scale of up to several millimeters depth in spite of the fact that they were continually, though very slowly, physically abraded by eolian processes (e.g., Hurowitz et al. 2006). Thus, later in Martian geological history, it appears that the S cycle continued, but on a greatly diminished scale and at a greatly diminished rate.

There are a number of possibilities to explain the origin of the acidity required for younger alteration. Evidence that some level of volcanism continued essentially through to the recent period includes Late Amazonian magmatic crystallization ages for most Martian meteorites and crater counts indicating volcanic surfaces perhaps as young as a few million years old. Some degassing would likely take place during such activity, although formation of acids from these reduced gases might be limited by availability of atmospheric oxidants (Zolotov 2007). Another possible source is through impact recycling of sulfate-bearing soils and sedimentary rocks (McLennan et al. 2006, Zolotov 2007). On Earth, the Late Cretaceous Chicxulub impact, which includes sulfate minerals in the target rocks, is thought to have resulted in formation of sulfuric acid vapor that was widely distributed in the atmosphere (e.g., Pierazzo et al. 1998), and a comparable event on Mars could produce as much as a 2-mm layer of H_2SO_4 over the entire Martian surface. The S-rich Martian regolith is one potential target, although the regolith is likely everywhere less than a few hundred meters in depth (e.g., Hartmann and Barlow 2006), and S recycling from impact into regolith would accordingly be less efficient, on average. Another potential target could be ancient S-rich sedimentary rocks, such as the Burns Formation. A final potential source of acidity could be oxidation of ferrous sulfates to ferric sulfates and iron oxides, as discussed in the next section.

Fe–S–O Cycles

Using orbital spectroscopy a number of workers have noted a spatial correlation between iron oxide and sulfate minerals on the Martian surface, indicating a possible genetic link (e.g., Bibring et al. 2007, Murchie et al. 2009, Roach et al. 2010). This relationship is also consistent with experimental and modeling studies that indicate a potential diagenetic transformation of ferrous sulfates to iron oxides under Martian surface conditions (McLennan et al. 2005; Tosca et al. 2005; 2008a; Sefton-Nash and Catling 2008). Tosca et al. (2008a) experimentally examined ferrous sulfate (melanterite; $FeSO_4{\cdot}7H_2O$) oxidation in high–ionic strength fluids and demonstrated a number of mineralogical pathways involving dissolution/precipitation, oxidation, hydrolysis, and dehydration, leading ultimately to ferric oxide (hematite) formation. Depending on specific conditions, intermediate steps included a diverse array of mixed valence sulfates (e.g., copiapite), ferric sulfates (e.g., ferricopiapite), and complex ochres (e.g., jarosite, schwertmannite, ferrihydrite). A simplified version of the reaction pathways is shown in Figure 5. These observations and experiments thus indicate a fundamental linkage between the Fe, O, and S cycles during surficial processes on Mars.

One example of a possible reaction pathway involving oxidation of aqueous ferrous iron ⇒ ferric iron ⇒ schwertmannite [$FeO(OH)_{0.75}(SO_4)_{0.125}$] ⇒ goethite [$FeO(OH)$] ⇒ hematite ($Fe_2O_3$) is illustrated in reactions 1 through 5 below (Tosca et al. 2008a, Hurowitz et al. 2010):

$$0.5H_2O + h\nu \Leftrightarrow 0.25O_2 + \mathbf{H^+} + e^- \tag{1}$$

$$Fe^{2+}_{aq} + 0.25O_2 + \mathbf{H^+} \Leftrightarrow Fe^{3+}_{aq} + 0.5H_2O \tag{2}$$

$$\begin{aligned} &Fe^{3+}_{aq} + \mathbf{0.125SO_4^{2-}} + 1.75H_2O \\ &\quad \Leftrightarrow FeO(OH)_{0.75}(SO_4)_{0.125} + \mathbf{2.75H^+} \end{aligned} \tag{3}$$

$$\begin{aligned} &FeO(OH)_{0.75}(SO_4)_{0.125} + 0.25H_2O \\ &\quad \Leftrightarrow FeO(OH) + \mathbf{0.25H^+} + \mathbf{0.125SO_4^{2-}} \end{aligned} \tag{4}$$

$$FeO(OH) \Leftrightarrow 0.5Fe_2O_3 + 0.5H_2O \tag{5}$$

These reactions provide mechanisms both for producing acidity and for recycling sulfur in surficial environments. For example, in the above reactions, for every mole of iron oxidized, converted to schwertmannite, and then oxidized/dehydrated to form hematite, 3.0 moles of H^+ are produced and 0.125 moles of S are recycled through the system. Accordingly, such reaction pathways provide potential sources of acidity both for early groundwater diagenesis, such as that observed at Meridiani Planum (e.g., Hurowitz et al. 2010), and both acidity and sulfur for formation of younger alteration surfaces on exposed rocks (e.g., Hurowitz et al. 2006).

SEDIMENTARY PROCESSES

Constraints on sedimentary geochemical processes that have operated on the surface of Mars over geological time come from four basic approaches. The first approach employs mission data that provide direct evidence for mineralogy and geochemistry in addition to stratigraphic relationships and, for the MER rovers, ~100-µm–resolution microtextural relationships from a microscopic imager. However, such data have several significant drawbacks. The *Spirit* and *Opportunity* rovers provide abundances for major and a few trace elements, quantitative constraints on iron mineralogy from Mössbauer spectroscopy, and additional but less well-constrained mineralogical information from thermal emission and visible through near-infrared spectroscopy. However, these methods “interrogate” rock surfaces on different lateral and depth scales, and, of fundamental significance, none of the methods allows for correlating geochemical or mineralogical data to textural information. Orbital spectroscopy and imaging allow for evaluation of correlations between mineralogy and stratigraphic relationships at ever-increasing resolution, but in many cases, quantitative evaluation of mineralogical abundances is difficult. Geochemical mapping by gamma ray and neutron spectroscopy operates at orders of magnitude lower spatial resolution but interrogates up to several tens of centimeters in depth, whereas infrared spectroscopy can have <10 m of spatial resolution but only interrogates the uppermost few microns of surfaces.

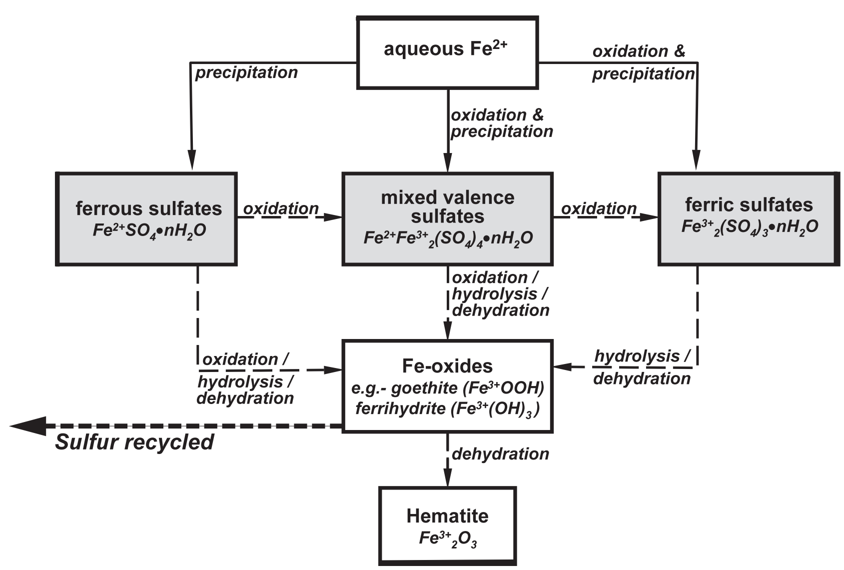

FIG. 5.—Major reaction pathways that may have been operating on Mars involving iron oxidation and precipitation in low-pH and sulfate-rich environments (adapted from Tosca et al. 2008a). Depositional processes are shown with solid arrows, and diagenetic reactions are shown with dashed arrows. Note that the transformation of iron sulfates to oxides involves liberation of sulfur that could be recycled back into the sedimentary system.

The second approach relies on a variety of laboratory experiments that have examined aqueous alteration, evaporation, and diagenetic processes. In these studies, experiments attempt to simulate rock, mineral, and fluid compositions and physico-chemical conditions thought to be relevant to Mars. The experimental results can then be used to test models by comparing results to chemical and mineralogical data obtained from the Martian surface. To date, there have been a number of studies that have explored acid alteration under Mars conditions (e.g., Tosca et al. 2004, Golden et al. 2005, Hurowitz et al. 2005, Tosca and McLennan 2009) but none that have yet explored the more modest conditions implied by recent discovery of clay minerals.

A third approach is to use basic thermodynamic and kinetic aqueous modeling tools to help constrain sedimentary processes under conditions relevant to Mars. Many of the modeling tools that are widely available often require significant adjustments to thermodynamic databases to accommodate differing conditions on Mars. For example, evaporation modeling of terrestrial systems does not typically consider iron because of the low concentrations in most aqueous fluids. However, on Mars, where low pH conditions prevailed, it is important to incorporate thermodynamic data for a variety of potential ferrous and ferric sulfate, carbonate, and chloride minerals (Tosca et al. 2005). Specialized aqueous modeling tools, such as FREZCHEM, have also been developed to deal with very low temperature conditions that prevail on Mars today (e.g., Marion et al. 2010).

A final approach is to examine geological and geochemical relationships in terrestrial settings that are thought to represent good analogs for comparable settings on Mars. The physico-chemical conditions that operate on Mars are likely sufficiently different (e.g., Tosca et al. 2011) that terrestrial settings constitute only partial analogs of some aspects of the chemistry and/or mineralogy being considered. Good examples are acid mine drainage systems and acid lakes that have been used as analogs for low pH conditions on Mars (e.g., Fernándes-Remolar et al. 2005, Baldridge et al. 2009). Important similarities in chemistry and mineralogy are observed, but in these cases the geological settings are not good analogs for what is observed on Mars.

Weathering

The red coloration of the Martian surface has long provided an obvious indication that some form of secondary alteration has influenced the surface of the planet (e.g., Burns 1993). The chemical compositions of soils at the Viking landing sites, including high S and Cl contents, were best modeled as representing mixtures of silicate minerals and sulfate/chloride salts (Clark 1993), further indicating that some form of aqueous alteration had been at work. More recent work (McSween et al. 2010) used a combination of chemical mass balance and spectroscopic observations to model Meridiani and Gusev soils as mixtures of approximately 70 to 85% igneous components (mainly plagioclase, pyroxene, olivine, oxides, and phosphates) and approximately 15 to 30% of an alteration assemblage (variable mixtures of sulfates, silica, clays, secondary oxides, and chlorides).

The exact processes involved in aqueous alteration have long been a matter of contention, with a variety of low-temperature (e.g., weathering, evaporites, iron formation, crater lakes) through intermediate- and high-temperature (e.g., acid fogs, palagonitization, hydrothermal alteration) models being proposed. More recent identification of Mg-, Ca-, and Fe-sulfate–cemented sandstones containing amorphous silica and altered basalt components at Meridiani Planum (Squyres et al. 2004, Clark et al. 2005, McLennan et al. 2005, Glotch et al. 2006), and with a mineralogy similar to that predicted by experimental and theoretical modeling studies of low-pH basalt alteration, coupled with orbital remote sensing observations for a wide variety of secondary minerals of likely sedimentary origin (sulfates, amorphous silica, clays, and possibly chlorides) pointed to a strong influence from a chemically dynamic sedimentary rock cycle (McLennan and Grotzinger 2008).

The chemical composition of Martian sedimentary materials strongly indicates a number of fundamental differences from terrestrial sedimentary environments. The issue of an overwhelmingly basaltic provenance was discussed above. This has profound implications both for the chemical and mineralogical composition of clastic sediments and for the composition of Martian natural waters. Figure 6 shows a ternary diagram plotting mole fractions Al_2O_3–(CaO+Na_2O+K_2O)–(FeO_T+MgO), or A-CNK-FM, which is commonly used to evaluate weathering and mixing processes in basaltic systems (Nesbitt and Wilson 1992). Under the circum-neutral pH conditions typical of terrestrial weathering, aluminum and ferric iron are insoluble, leading to Al- and Fe-depleted natural waters and weathering residues that are concentrated in these elements (Fig. 6a, c). Siliciclastic sediments in turn are also enriched in weathering residues (i.e., clays and iron oxides), with chemical sediments forming from the dissolved constituents (for basalts, dominated by Ca, Mg, and Na). Thus, terrestrial weathering profiles and the siliciclastic sediments derived from them typically have compositions that scatter above the feldspar–(FeO_T+MgO) join on the A-CNK-FM diagram.

In contrast, and with only a very small number of exceptions, Martian sedimentary materials that have been analyzed to date, including soils, altered rock surfaces, and sedimentary rocks, scatter parallel to but below the feldspar–(FeO_T+MgO) join. This trend has been used to suggest that acidic alteration dominated, such that mafic mineral dissolution (e.g., dissolution of olivine, Fe-Ti oxides, pyroxene, glass), rather than mineral alteration to clays, was the major process (Fig. 6d). The lack of evidence for significant Al mobility, for example, as Al-sulfates, that would be expected in low-pH environments led Hurowitz and McLennan (2007) to suggest that low water–rock ratios were involved, such that only the most soluble minerals (i.e., olivine but not plagioclase) were mainly affected. Such an interpretation is also consistent with low-pH aqueous alteration experiments on Martian basalt compositions (e.g., Tosca et al. 2004; Golden et al. 2005; Hurowitz et al. 2005, 2006).

One potential complication to these interpretations is that most of the materials shown in Figure 6b, unlike those shown for the terrestrial examples (Fig. 6a), include both siliciclastic and chemical (mainly sulfate) constituents that are mixed together in various proportions, thus potentially obscuring any terrestrial-like geochemical weathering trends that might exist (McLennan 2010). Mineralogical constraints are simply too uncertain and nonquantitative to unambiguously distinguish small amounts of an aluminous residual component. Another factor, described above, is that more recent evidence indicates that sulfate-rich sedimentary rocks appear to be characteristic of younger Late Noachian–Hesperian terrains, whereas clay-rich exposures dominate in the earlier Noachian. If correct, this might also indicate that weathering regimes have evolved over geological time.

Regardless of exact aqueous conditions, the discovery of extensive exposures of clay-bearing strata in Noachian terrains indicates that weathering processes have been operating in some form essentially throughout recorded Martian geological time. There is considerable diversity in the apparent composition of Noachian clays, but they appear to be dominated by Fe-Mg smectites (e.g., nontronite) with lesser aluminous smectites and highly aluminous kaolinite. The exact origin of the Noachian clay mineral suites is not well constrained and could be due to some form of pedogenic weathering, in situ alteration (e.g., analogous to terrestrial bentonites), diagenesis, and/or hydrothermal alteration associated with volcanic centers and large impact craters. Accordingly, the implications for the nature of Noachian weathering processes are also not yet well constrained. Assuming that these clays are at least in part the result of surficial weathering processes, the predominance of Fe-Mg smectites might indicate

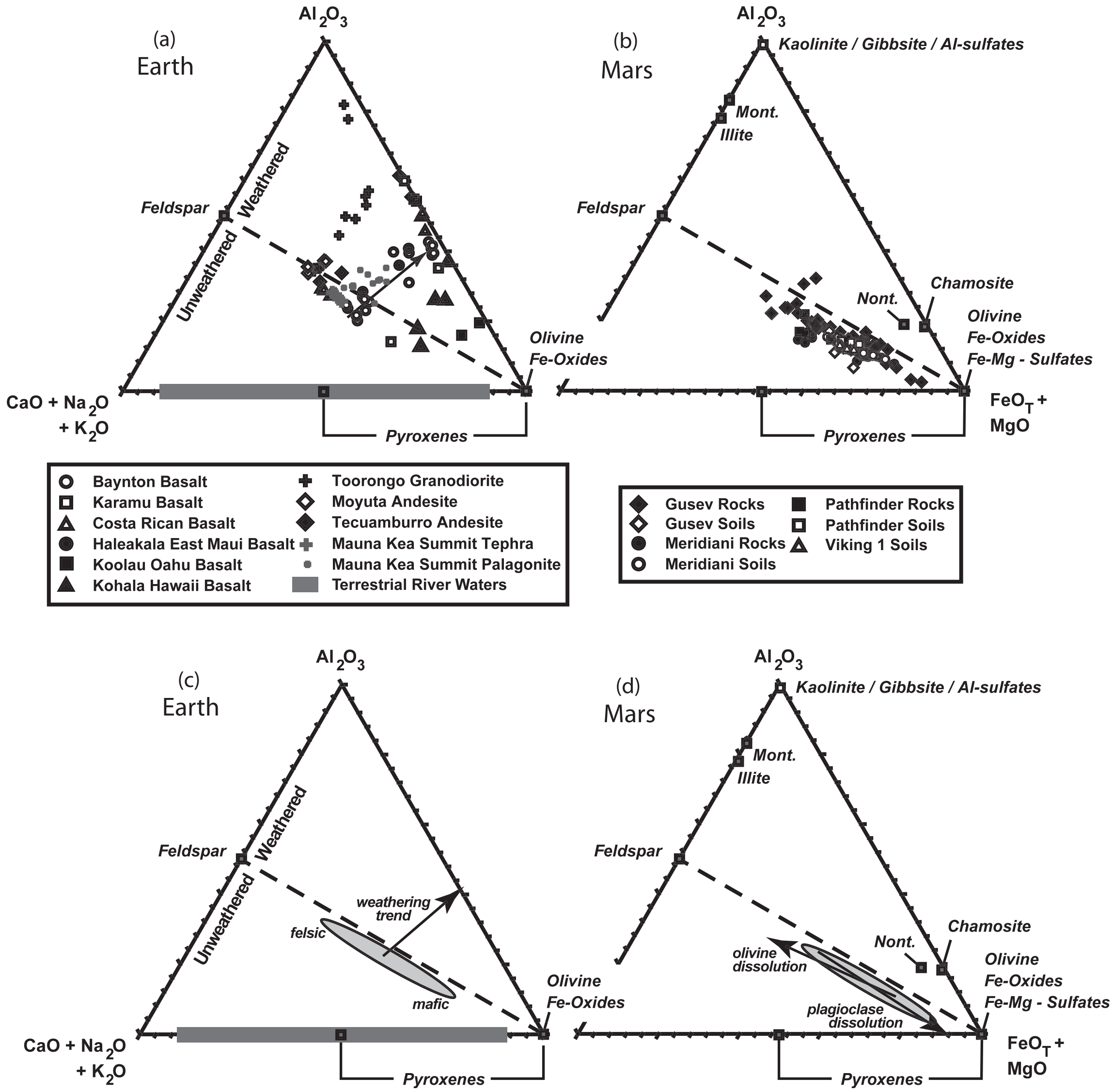

FIG. 6.—A-CNK-FM ternary diagrams plotting molar proportions of Al_2O_3–(CaO+Na_2O+K_2O)–(FeO_T+MgO). Typical compositions for some major igneous and sedimentary minerals are plotted; note that the dashed diagonal line in each diagram separates regions of the diagram dominated by primary igneous silicate minerals (unweathered) from the area dominated by clay minerals (weathered). (a) Selected samples from weathering and alteration profiles in terrestrial settings, emphasizing basaltic–andesitic terrains. Note that in all cases increased alteration results in enrichment in Al and Fe as a result of their insoluble character and concentration in residual clays and oxides. (b) Available data for Martian soils, rocks, altered rock surfaces, and sedimentary rocks (n ~ 200). Note that almost all Martian data fall below and parallel to the diagonal dashed line in spite of evidence for alteration in many of the samples. (c) Field illustrating compositional variation in primary terrestrial igneous rocks, with an arrow showing a typical terrestrial weathering trend. (d) Field illustrating compositional variation in primary Martian mafic to ultramafic igneous rocks. Arrows show alteration trends for olivine dissolution and plagioclase dissolution from typical basalt composition. The differing trends observed for terrestrial and Martian global alteration patterns have been explained by low-pH, low water–rock ratio conditions on Mars, such that mineral dissolution dominates over alteration to clays. Adapted from Hurowitz and McLennan (2007).

relatively low water–rock ratios since in well-drained basaltic weathering environments, aluminous clays, notably kaolinite, would be expected (e.g., White 1995, van der Weijden and Pacheco 2003). Yet another possibility is that such smectites, although ultimately formed in low water–rock environments, could be later transported and deposited in water-dominated fluvial or lacustrine environments.

Depositional Processes

Many contributions, including a number of those to this volume, illustrate the wide diversity of both subaerial and subaqueous depositional environments that have been recognized on Mars, including eolian, fluvial, deltaic, glacial, lacustrine, and possibly fan settings. However, in situ major and trace element data are only available for clastic sedimentary rocks at two landing sites (Gusev and Meridiani), with only Meridiani being well characterized for sedimentology and stratigraphy, and, accordingly, the constraints that geochemistry provide are limited. Some insight regarding the influence of various sedimentary processes (e.g., weathering, sorting) can be obtained from the study of unconsolidated Martian soils (e.g., McLennan 2000, Yen et al. 2005, Karunatillake et al. 2010, McSween et al. 2010), but soils are of broadly uniform composition (although with some influence from local geology), and the limited variation makes it difficult to unravel any competing influences of provenance from processes. It is also worth pointing out that the number of studies of terrestrial systems that have examined source-to-sink geochemistry of sedimentary basins that are dominated by basaltic provenance are remarkably few (e.g., van de Kamp and Leake 1985, 1995; Saha et al. 2010), and from the perspective of understanding Mars, this represents a fruitful area for further research.

One area that has received considerable attention is the nature of evaporitic depositional processes on Mars.[2] This is because fluid evaporation, unlike clastic sedimentation, involves to a much larger degree equilibrium processes and accordingly is amenable to both experimental and thermodynamic modeling approaches. One of the major findings of the past decade is the recognition that evaporative processes have been a major depositional (and diagenetic) process for much of Martian geological time. Ancient sedimentary sequences, studied by both *Opportunity* and *Spirit*, possess abundant sulfate minerals, and from orbit, widespread sulfates have been identified in layered sequences; in addition, even exposures of possible chloride minerals have been observed.

Tosca and colleagues (Tosca et al. 2005, 2007, 2008b; Tosca and McLennan 2006) used Pitzer ion interaction thermodynamic models to constrain evaporation processes on Mars. Although such modeling techniques are well established in terrestrial settings, in order to apply them to Martian conditions it is necessary to incorporate an internally consistent thermodynamic database for a wide variety of Fe^{2+} and Fe^{3+} species. Figure 7 illustrates one example of such modeling and shows the mineralogical pathways (so-called chemical divides; see Hardie and Eugster 1970, Eugster and Jones 1979) for the evaporation of a single basaltic brine having a composition derived from acid weathering of olivine-bearing basalt and with varying initial pH governed by variable HCO_3^-/SO_4^{2-} ratios. Because Martian brines are likely sulfate-rich; enriched in Mg, Ca, and Fe; and depleted in Na and K—unlike terrestrial seawater, which is chloride-rich; elevated in Ca, Mg, Na, and K; and devoid of Fe—the evaporation pathways for typical Martian brines and terrestrial seawater differ greatly (Table 4).

It is notable that the numerous possible evaporation pathways in Figure 7 lead only to a limited number of late-stage brine compositions, which is similar to what is seen in terrestrial systems. Also of note is the fact that the two distinct evaporite mineral associations observed on Mars, within the Burns Formation (Mg-, Ca-, Fe^{3+}-sulfate; possibly halite) and within fractures in Martian nakhlite meteorites (siderite, gypsum, sulfates, chlorides) (Bridges and Grady 1999), can be explained by the same basaltic brine but with differing initial anion chemistry (HCO_3^-/SO_4^{2-}) and thus differing initial pH. Some caution is warranted since neither of these examples represent equilibrium assemblages. On the other hand, they probably do provide some constraints on the nature of the fluids involved. Tosca and McLennan (2006) suggested that the evaporite minerals in Burns Formation were formed by low-pH acid–sulfate surface waters, whereas the assemblages within fractures in Martian basaltic meteorites likely formed from fluids out of contact with the surface environment and thus buffered by basalt–fluid interaction.

McLennan (2003) pointed out that aqueous alteration of basaltic rocks efficiently produces excess silica in solution, and so sedimentary silica should be common on Mars. Simple mass balance of typical mafic mineral weathering reactions indicates that there should be very approximately 1 mole of SiO_2 for each mole of sulfate formed from reaction of sulfate with various cations released by the alteration process (Fig. 8). Although spectral libraries did not at the time adequately represent amorphous silica, quartz, the typical diagenetic product of opaline silica maturation (e.g., Knauth 1994), had not been detected at any significant level. Spectral libraries have greatly improved and secondary amorphous silica has now been identified, using in situ geochemistry and infrared spectroscopy, in the sedimentary rocks of the Burns Formation (Glotch et al. 2006) and as likely hydrothermal deposits in Gusev Crater (Squyres et al. 2008, Ruff et al. 2011). Orbital remote sensing has also identified amorphous silica in a variety of geological settings on the Martian surface (Milliken et al. 2008, Bishop et al. 2009, Murchie et al. 2009).

The scale, nature, and depositional processes of any carbonate sedimentary reservoir remains largely unknown. Fe-Mg-Ca carbonates have been observed in Martian meteorites, notably the 1.3 Gyr nakhlites and the 4.1 Gyr ALH84001, as secondary mineral assemblages in veins and interstitial areas (McSween and Harvey 1998, Bridges and Grady 1999, Bridges et al. 2001). Polar soils at the Phoenix landing site show evidence for about 3 to 5% $CaCO_3$ (Boynton et al. 2009), and a small carbonate component (2–5%) of uncertain mineralogy, but possibly $MgCO_3$, has been identified in Martian dust from orbital spectroscopy (see review in Christensen et al. [2008]). Other identifications of carbonate minerals both from orbit (Ehlmann et al. 2008) and from in situ observations by the Spirit Rover (Morris et al. 2010) indicate the presence of carbonates, but most likely in hydrothermal settings.

Diagenetic Processes and Recycling

It is now reasonably well established that water-mediated diagenesis has taken place on Mars, perhaps over much of its geological history, although at highly variable rates. One of the major findings from the Burns Formation at Meridinai Planum was unambiguous textural, mineralogical, and geochemical evidence for syn- to postdepositional diagenetic overprints involving a fluctuating groundwater table (Squyres et al. 2004, Grotzinger et al. 2005, McLennan et al. 2005). Among the major processes recorded (from oldest to youngest) were syndepositional crystallization, perhaps at the capillary fringe, of a cross-cutting highly soluble evaporite mineral; formation of pore-filling cement; formation of millimeter-scale uniformly distributed hematitic concretions; dissolution of the previously precipitated cross-cutting evaporite mineral and early-formed cements to form secondary crystal mold and sheet-like vug secondary porosity, respectively; formation of late cements overgrowing concretions; and nodular features related to recrystallization. When diagenetic stratigraphy is coupled with sedimentological constraints (Grotzinger et al. 2005, 2006; Metz et al. 2009), at least four distinct recharge events can be recognized during deposition and diagenesis. Tosca et al. (2004; also see Sefton-Nash and Catling [2008]) carried out geochemical modeling that further indicated that the groundwater was of very high ionic strength, low pH, and derived from the weathering of olivine-bearing basalt.

As pointed out above, a number of workers have noted a correlation between the distribution of iron oxides and sulfate minerals on the Martian surface using orbital spectroscopy (e.g., Bibring et al. 2007, Murchie et al. 2009, Roach et al. 2010). This relationship is consistent

[2]In the context of Mars, evaporites could form when natural waters either evaporate or freeze. Exact mineral and geochemical evolution pathways may differ slightly for these processes, but for this work only evaporation is considered, both because early Mars is often thought to have been "warmer and wetter" and because most experimental and theoretical modeling research has been carried out on the evaporation process.

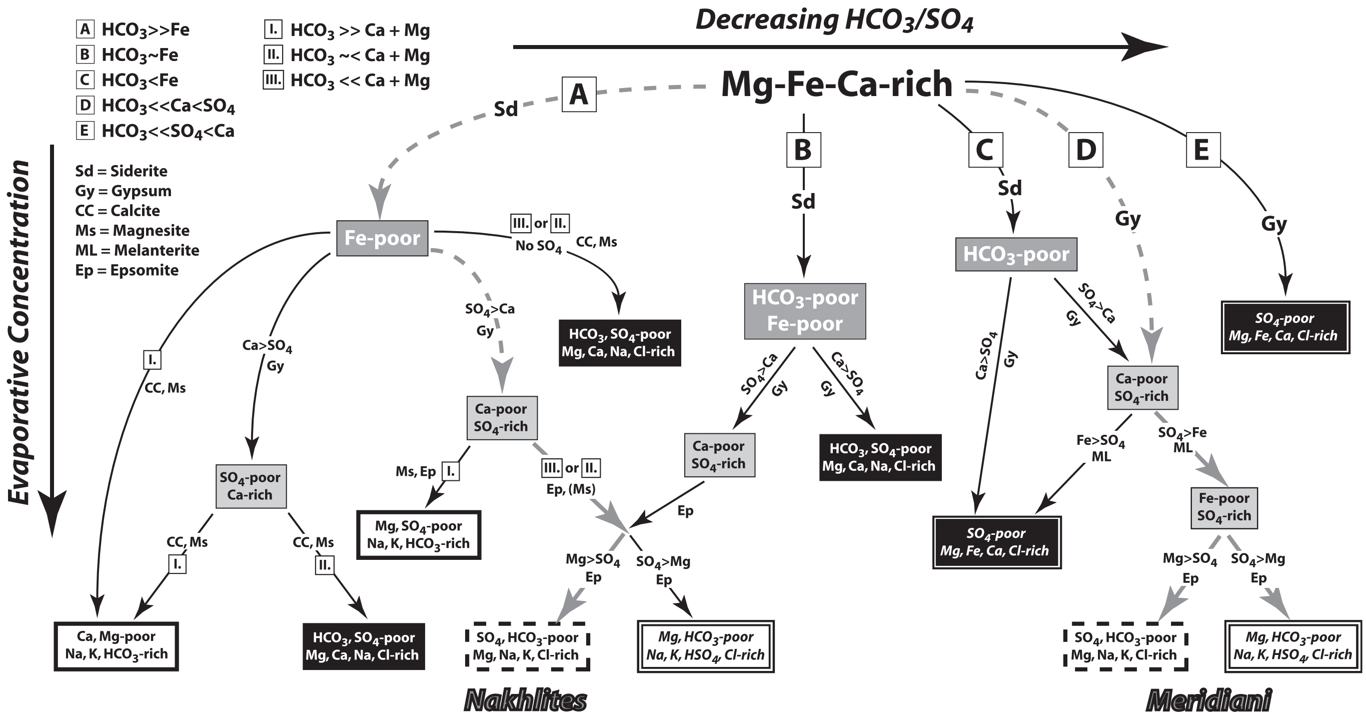

FIG. 7.—Flowchart illustrating chemical and mineralogical evolution (chemical divides) of an evaporating fluid derived by low-pH weathering of an olivine-bearing basalt. A single brine cation composition is modeled, with evaporative concentration increasing downward and the ratio of HCO_3^-/SO_4^{2-} (i.e., initial pH) decreasing to the right. The chemical characteristics of the latest-stage brines are described in the boxes that terminate each evaporation pathway. Although nearly 20 evaporation pathways are possible, only five distinctive end-stage brines result, which is similar to that seen for the evaporation of terrestrial brines. Possible evaporation/mineral precipitation pathways for Meridiani Planum evaporite mineralogy (heavy dashed gray lines on the right-hand side) and evaporite mineral assemblages in the Nakhla meteorites (heavy dashed gray lines on the left-hand side of the diagram) are shown. Figure adapted from Tosca and McLennan (2006).

TABLE 4.—Comparison of the order of precipitation of evaporite mineral sequences for terrestrial seawater and a potential Martian brine.[1]

Seawater			Mars brine	
		First crystallized		
Aragonite	($CaCO_3$)		[Siderite][2]	[($FeCO_3$)]
Gypsum	($CaSO_4·2H_2O$)		Gypsum	($CaSO_4·2H_2O$)
Halite	(NaCl)		Melanterite[3]	($FeSO_4·7H_2O$)
Epsomite	($MgSO_4·7H_2O$)		[Magnesite][2]	[($MgCO_3$)]
Kainite	($KClMgSO_4·3H_2O$)		Epsomite	($MgSO_4·7H_2O$)
Carnallite	($KMgCl_3·3H_2O$)		Halite	(NaCl)
Bischofite	($MgCl_2·6H_2O$)		Other late-stage bittern salts[4]	
Other late-stage bittern salts				
		Last crystallized		

[1] Various dehydration effects (e.g., gypsum ⇒ anhydrite; epsomite ⇒ hexahydrite ⇒ kieserite, etc.) not included.
[2] Siderite and magnesite are predicted to precipitate only for fluids with relatively high HCO_3^-/SO_4^{2-} ratios and thus higher initial pH.
[3] Melanterite forms when brine is nonoxidizing. Depending on how oxidized the brine is, various ferric sulfates (e.g., copiapite, bilinite, jarosite) are also predicted to precipitate both before and/or after epsomite precipitation (Tosca et al. 2008).
[4] Evaporation modeling of Martian brines has not been taken beyond halite precipitation.
References: Warren (2006), Tosca and McLennan (2006), and Tosca et al. (2008b).

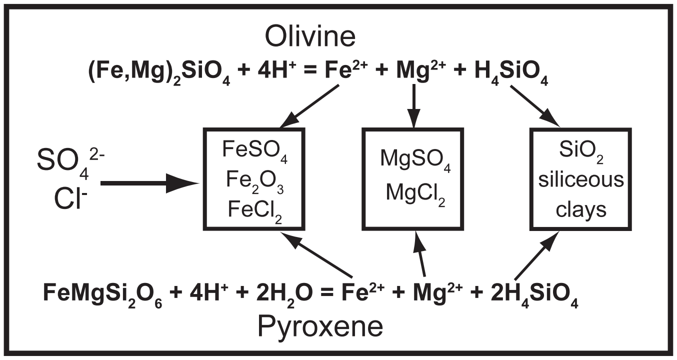

FIG. 8.—Schematic diagram illustrating the mass-balance arguments to indicate that secondary silica should be common on Mars if basalt is altered and sulfate/chloride minerals are precipitated from resulting fluids. Alteration of olivine and pyroxene results in the release of approximately 1 to 2 moles of silica (typically as silicic acid or related species) for each mole of mineral dissolved. Adapted from McLennan (2003).

with experimental and modeling studies that indicate a diagenetic transformation of ferrous sulfates to ferric sulfates and ultimately to iron oxides under Martian surface conditions (McLennan et al. 2005; Tosca et al. 2005, 2008a; Sefton-Nash and Catling 2008; also see Navrotsky et al. [2005], Golden et al. [2008]). Tosca et al. (2008a) showed one likely mineralogical pathway with schwertmannite and jarosite as intermediate steps (Fig. 5). As discussed further below, the observation that ferric sulfates have not more completely transformed to iron oxides appears to indicate a water-limited process. Nevertheless, in addition to providing a recycling mechanism for sulfur (see above), such a process could represent a pathway for very slow, incremental oxidation of the Martian near-surface environment over geological time (i.e., during the Siderikian era of Bibring et al. [2006]).

Although it is clear that aqueous diagenesis has occurred, an equally interesting characteristic of the Martian sedimentary record is the apparent dearth of diagenetic changes under conditions during which such reactions might be expected. Tosca and Knoll (2009) described sedimentary assemblages as being "juvenile and diagenetically underdeveloped," based on modeling of temperature–time integrals (Siever 1983) for Martian sedimentary basins under a wide range of possible burial conditions. Three observations are especially notable:

1. Persistence of iron sulfates, notably of jarosite within the Late Noachian–Early Hesperian Burns Formation, in spite of it being metastable with respect to goethite and hematite over a broad pH range (Elwood Madden et al. 2004; also see Berger et al. [2009]). Comparisons with laboratory and field data, such as at Rio Tinto, indicate that groundwater could only have been present for $<10^4$ years, and perhaps as little as 10^1 years, after jarosite formation.

2. Predominance of Fe- and Mg-rich smectitic clays (e.g., nontronite, saponite) over more mature aluminous clays (e.g., kaolinite, montmorillonite) in Noachian terranes. In terrestrial settings, smectites diagenetically transform in the presence of water to either illite or chlorite, depending on composition, with timescales depending on thermal conditions of burial, but typically <400 Myr. The persistence of these diagenetically immature clay mineral assemblages for about an order of magnitude more time than this is thus consistent with limited postdepositional interaction with water.

3. Perhaps the most remarkable observation related to sediment diagenesis is the apparent absence of any recrystallization of amorphous silica to form quartz, despite being in places inferred to be of Noachian–Hesperian age (e.g., Glotch et al. 2006, Squyres et al. 2008, Ruff et al. 2011). Quartz has distinctive infrared spectral properties such that it can be identified from remote sensing with confidence at the few percent level (e.g., Bandfield et al. 2004). In terrestrial settings, amorphous silica rarely survives more than a few million years, with only very few occurrences being $>10^8$ years, before undergoing the Opal-A $\Rightarrow$ Opal-CT $\Rightarrow$ quartz transition. Modeling temperature–time integrals for basin evolution on Mars indicates that even under the most favorable circumstances, amorphous silica should survive on Mars for no more than about 400 Myr, or about an order of magnitude less than the oldest known occurrences. The most likely mechanism allowing for long-term persistence of amorphous silica is the absence of aqueous conditions (Tosca and Knoll 2009).

An area that has not received much attention is the strong potential for diagenetic recycling of evaporites on Mars. On Earth, evaporite deposits are dominated by gypsum and anhydrite, which are relatively insoluble. Late-stage evaporite minerals, including halite and the various bittern salts, are far less abundant and highly prone to dissolution and recycling back into the aqueous environment. Analogous processes have not been considered for Mars. Figure 9 shows the effects of interacting a typical Martian evaporite assemblage with dilute waters, and, not surprisingly, very small amounts of water–mineral interaction result in complete dissolution of Mg- and Fe-sulfates and halite, with virtually no effect on gypsum.

One implication of this is that the relatively high abundance of highly soluble sulfates and possibly chlorides exposed at the surface of Mars limits the amount of interaction with relatively fresh waters since the time of deposition. Any later fluids that interacted with earlier-

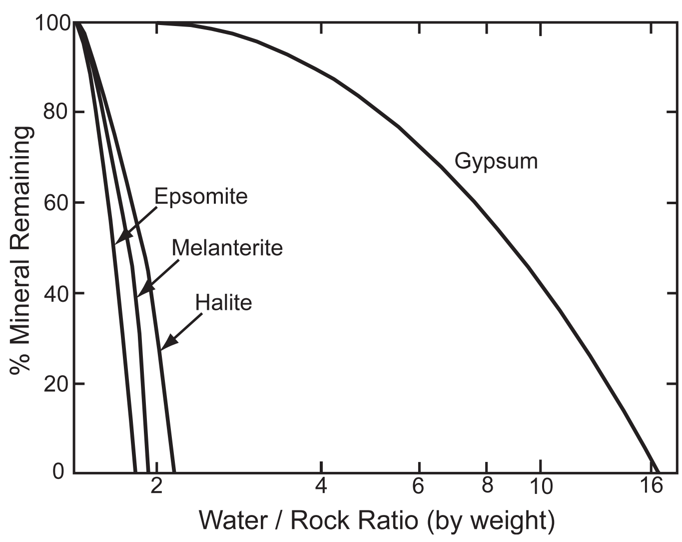

FIG. 9.—Plot of amount of mineral remaining vs. water–rock ratio for the interaction of a potential Martian evaporite mineral assemblage with pure water, using published mineral dissolution rates (see Hurowitz and McLennan [2007] for general approach). Apart from gypsum, Martian evaporite minerals are highly soluble, and at the point of complete dissolution of epsomite, melanterite and halite, $<1\%$ of the gypsum has dissolved. Accordingly, diagenetic interaction of Martian evaporites with any relatively fresh water after deposition has the potential to result in strong mineralogical fractionation of gypsum from the other evaporite minerals.

formed Martian evaporite assemblages would also have mostly evolved to late-stage brines. This in turn could also have astrobiological implications. Thus, Tosca et al. (2008b) suggested that the implied low water activity (a_{H2O}) of late-stage Martian brines inhibits habitability.

A second implication is that wherever diagenetic water–mineral interaction did take place, it could provide an efficient mechanism for separating relatively insoluble gypsum from other evaporite minerals. Effectively, gypsum becomes a residual mineral, which then could be preferentially recycled and concentrated by physical processes. One example where this might be relevant is in the enormous gypsum-bearing north polar ergs (Langevin et al. 2005, Fishbaugh et al. 2007, Horgan et al. 2009, Szynkiewicz et al. 2010). These deposits have been mostly interpreted as forming by depositional processes during which gypsum is initially produced in playas or near-surface groundwater and then transported by eolian processes, such as at White Sands, New Mexico (e.g., Szynkiewicz et al. 2010), or gypsum is produced by direct precipitation (related to either alteration or evaporation) from fluids percolating through the dunes themselves (e.g., Fishbaugh et al. 2007). However, another possible scenario could be related to diagenetic processes, whereby gypsum is separated from other evaporitic minerals in the near-surface environment through interaction with very small quantities of water and is then physically recycled by eolian processes.

DISCUSSION

Although remarkable progress has been made in understanding the nature of the Martian sedimentary record, especially over the past decade, there is still much that is unknown and even more that is uncertain. For example, on Earth there are good quantitative constraints on the lithological and chemical composition of the sedimentary rock record through geological time, and this provides crucial evidence for understanding how the terrestrial sedimentary mass forms and evolves (e.g., Garrels and Mackenzie 1971; Veizer and Jansen 1979, 1985; Ronov 1983; Taylor and McLennan 1985, 2009; Veizer and Mackenzie 2003). For Mars, we are just beginning to take an inventory of the sedimentary materials, and anything approaching a quantitative understanding is likely many years away. Nevertheless, considerable insight into conditions of Martian surficial processes is possible. Accordingly, in the following sections, several of the major issues related to the Martian sedimentary rock cycle that can be constrained from the geochemical data are discussed. Each of these issues provides rich opportunities for further research.

Size and Constitution of the Martian Sedimentary Mass

Is it possible to place some geochemical constraints on the overall size of the sedimentary mass and its various lithological reservoirs? As discussed above, the amount of sulfur in the surficial environment is likely on the order of at least 10^{21} to 10^{22} g. For the following discussion, the lower sulfur value of 10^{21} g is adopted to simplify calculations and to provide what is considered a reasonable lower limit. However, the likely range allows for values an order of magnitude or more higher. Assuming that all of this surficial sulfur is tied up in sulfate minerals with an average global hydrated sulfate mineral formula of $Fe_{0.4}Mg_{0.4}Ca_{0.2}SO_4{\cdot}2H_2O$, with cation proportions based on their relative amounts in Martian crust (Taylor and McLennan 2009), this translates into a sulfate mineral reservoir of approximately 5.5×10^{21}g, or about 0.2% of the terrestrial sedimentary mass (for reference, the terrestrial sedimentary mass is $\sim 2.7 \times 10^{24}$ g; Veizer and Mackenzie 2003). Adopting the average Martian soil S/Cl mass ratio of 3.6 (Taylor and McLennan 2009), a chloride reservoir (assuming a 50:50 mix of NaCl and $Mg_{0.67}Ca_{0.33}Cl_2$) is calculated to be 2×10^{20} g. The formation of secondary silica is strongly tied to the breakdown of mafic minerals, such as that shown in Figure 8 (McLennan 2003). Assuming that approximately 1 mole of silica is formed for each mole of sulfate or chloride that is formed, a secondary silica (assuming $SiO_2{\cdot}1.5H_2O$) reservoir of approximately 2×10^{21} g is also estimated. Although it is known that carbonate minerals exist on Mars, their overall abundances thus far appear to be trivial, and, accordingly, a carbonate sedimentary reservoir is assumed to be negligible. Thus, the total amount of sulfate, chloride, and silica is calculated as being between about 8×10^{21} and 8×10^{22} g, and this represents a likely minimum estimate of the chemical constituents in the Martian sedimentary mass.

In terrestrial sedimentary systems, there are several lines of evidence that can be used to constrain the relative proportions of the chemical constituents to the overall size of the sedimentary mass. For example, Millot et al. (2002) evaluated the empirical relationship between chemical (R_{Chem}) and physical (R_{Phys}) weathering rates in a wide variety of geological settings such that

$$R_{Chem} = 0.39R_{Phys}^{0.66} \quad (6)$$

which, if applied to the overall Martian sedimentary record (an assumption, since no such relationship has yet been documented for Mars), indicates a ratio of detrital to chemical constituents of about 3:1. This is comparable to the relative proportions of detrital to chemical constituents in modern terrestrial rivers and in the overall terrestrial sedimentary rock record, for which the ratios are estimated to be about 4:1 and 6.5:1, respectively (Garrels and Mackenzie 1971, Henderson and Henderson 2009). In addition, Stewart (1993) used chemical mass balance calculations to estimate the ratio for 13 rivers draining sedimentary rock terrains and derived a value of approximately 6:1. Impact processes, which would be dominated by particulate material, likely played a much more important role in forming the preserved sediment on Mars compared to Earth, where the >4.0 Gyr sedimentary record is missing. Finally, it is likely that pyroclastic activity, also generating large volumes of particulate debris, has been much more active on Mars than on Earth (Wilson and Head 1994). Accordingly, if we adopt a fairly conservative clastic to chemical ratio of 5:1, this indicates an overall minimum Martian sedimentary rock record of between about 5×10^{22} and 5×10^{23} g, or between about 2 and 20% of the size of the terrestrial sedimentary mass. These calculations, though highly preliminary, indicate that Mars likely has a very substantial sedimentary record, especially given that the surface area of Mars is only about one-third that of Earth and that sediment preservation associated with plate tectonic processes (e.g., Veizer and Jansen 1985) has not occurred.

A Fundamental Paradox: How Much Water?

The surface of Mars provides compelling geomorphological evidence, in the form of channels and subaqueous deltas, for large amounts of liquid water flowing on the surface early in its history. Secondary minerals (e.g., sulfates, clays, silica, chlorides) observed both within sedimentary rocks at the *Spirit* and *Opportunity* landing sites and from orbit also indicate that water-mediated surficial alteration processes were active in the formation and deposition of Martian sedimentary rocks. Thus, Bibring et al. (2006) proposed that the Martian surface was water-rich through to about the Mid-Hesperian. The Burns Formation preserved at Meridiani Planum shows clear evidence for a groundwater influence during both deposition and diagenesis, and a likely hydrothermal system has been recognized in the Inner Basin of the Columbia Hills. Thus, at first glance, early in Mars history it would appear that near-surface liquid water may have been rather abundant.

However, when the chemistry and mineralogy of the Martian sedimentary record are examined more closely, a very different picture emerges, leading to an apparent paradox. Chemical and mineralogical evidence indicates that most sedimentary materials that have been examined to date are best explained by low water–rock ratios. Some of this evidence can be summarized as follows:

1. Although the Burns Formation was influenced by groundwater, including evidence for phreatic (i.e., saturated) conditions (McLennan et al. 2005), other observations point to low water–rock ratios. Inferred mineralogy includes Mg-sulfates and possibly chlorides (e.g., Clark et al. 2005). The evaporation modeling of Tosca et al. (2008b) indicates that these minerals precipitate at very low water activities (i.e., $a_{H2O} < 0.78$ for epsomite; <0.5 for halite) and accordingly derive from concentrated brines. The mineralogy of these sedimentary rocks is thus highly labile, and preservation of submillimeter-scale laminations and textures (Grotzinger et al. 2005) indicates that they have never interacted with waters less dilute than those with a_{H2O} greater than about 0.8 since deposition (also see Fig. 9). The presence of jarosite also indicates that the groundwater system must have been short-lived (Elwood Madden et al. 2004, Berger et al. 2009).

2. The chemical data shown in Figure 6 indicate that, in comparison with Earth, the nature of surficial processes is fundamentally different on Mars (Hurowitz et al. 2006, Hurowitz and McLennan 2007), at least for certain parts of Martian geological time. The widespread apparent mobility of ferric iron implies low pH conditions. However, at these conditions aluminum is far more soluble than ferric iron. The Martian sedimentary record is replete with evidence for secondary iron phases that imply mobility (iron sulfates, secondary iron oxides) but thus far little evidence for secondary aluminum phases (e.g., aluminum sulfates) at the times represented by the rocks and soils plotted in Figure 6. Hurowitz and McLennan (2007) interpreted this to indicate that low-pH aqueous alteration processes operated at very low water–rock ratios, such that only the most soluble phases (e.g., olivine, phosphates, Fe-oxides, but not plagioclase) were dissolved before altering solutions were effectively buffered and became nonreactive.

3. Occurrences of ancient diagenetically immature mineral assemblages (iron sulfates, smectitic clays, amorphous silica) described above all point to very low water–rock ratios since the time of deposition (Tosca and Knoll 2009).

Paradoxes rarely reflect the true operations of nature but instead reflect insufficient understanding of the geological record. What are some possible explanations? One possibility is that liquid water flow on the early Martian surface was intermittent rather than continuous. This might indicate that the record of clay minerals preserved in the Noachian does not reflect a ubiquitous water-rich environment, as generally thought. Another possibility is that the transition from relatively water-rich (i.e., Phyllosian) to water-restricted (i.e., Theiikian or Siderikian) conditions was extremely abrupt, such that aqueous-mediated diagenetic processes were effectively inoperative or at least extremely sluggish once sediment had been deposited. This does not appear to be consistent with the detailed stratigraphic relationships that are observed. Thus, the Burns Formation, which records a dynamic groundwater table, likely was deposited during the Late Noachian to Early Hesperian, after the so-called Phyllosian era. Regardless of the exact explanation, these apparently contradictory observations demonstrate the need for further work both in the laboratory and on the surface of Mars.

Mars: A Planet on Acid?

It is now widely agreed that for much of Martian geological time, surficial processes operated under low-pH, acid-sulfate conditions. Some of the basic evidence (in no particular order) includes highly elevated sulfur concentrations in the near-surface environment; a dearth of carbonate minerals, especially in the ancient sedimentary record; widespread evidence for ferric iron mobility, despite the Martian surface appearing relatively oxidizing; the presence of evaporite mineral associations consistent with evaporation of low-pH, sulfate-rich waters; and igneous rock chemical/mineralogical alteration trends consistent with acid alteration experiments. However, the presence of widespread Noachian clays indicates more modest pH conditions at that time, and this provides the fundamental evidence for the concept of mineralogical eras proposed by Bibring et al. (2006). Trying to understand the global chemical regimes that gave rise to these differing conditions is a daunting task.

If indeed the sulfur cycle dominated the surficial processes on Mars it is perplexing to consider how that process could have been so different in the earlier Noachian. For example, there is no strong evidence for sedimentary carbonates associated with the clay-bearing sedimentary rocks (Milliken et al. 2009). Halevy et al. (2007) proposed that conditions were also more reducing, resulting in sulfite, rather than sulfate, being the dominant aqueous sulfur species. Under reducing conditions the sulfur cycle would give rise to acidic but more modest pH (i.e., sulfurous rather than sulfuric acids), thus balancing on the tightrope by being basic enough for clay formation but acidic enough to inhibit carbonate formation. Although somewhat ad hoc, the model in principle is testable since it predicts the formation of minerals that have not yet been detected (i.e., sulfites), but perhaps with better spectral libraries could be. On the other hand, this family of minerals may not survive through geological time (Halevy et al. 2007).

Another possibility is that the geological context, and thus the implications, of Noachian clays may not be fully understood. For example, it is not obvious that significant amounts of water are necessarily required to form the most abundant Noachian clay mineral suites, dominated by Fe/Mg-smectites. During typical basalt weathering, smectites tend to form during the earliest stages of weathering, with kaolinite dominating more advanced stages (e.g., Nesbitt and Wilson 1992). Accordingly, perhaps the Noachian clay assemblages represent incipient alteration involving small amounts of water. Such conditions might also be more consistent with the apparent absence of the complementary chemical constituents (Milliken et al. 2009).

A long-standing question related to the idea of low-pH aqueous conditions is that chemical interaction of such fluids with basaltic rocks should rapidly lead to a buffered circum-neutral pH, and, consequently, it is not possible to sustain acidic conditions. Tosca et al. (2005; also see Tosca and McLennan [2006]) pointed out that the very low pH expected for acid-sulfate waters requires orders of magnitude more rock interaction to buffer them than do the weakly acidic waters associated with the carbon cycle. In addition, evaporation of such fluids further lowers pH, and the overall evolution of the pH of the system is a competition between acid generation from sulfur addition (e.g., from volcanic gases or recycling) and evaporation and the buffering actions of weathering reactions.

Recent work by Hurowitz et al. (2010) on the Burns Formation indicates that low pH conditions may in fact be more localized than previously thought. Water–rock interaction of basalts, in addition to driving the system toward circum-neutral pH, leads to reducing conditions. Relatively reducing conditions would allow for the transport of ferrous iron in solution, and subsequent oxidation of iron produces significant amounts of acidity in the near-surface environment (also see Hurowitz et al. [2009]).

Perhaps the most important conclusion that can be drawn from the above discussion is that Martian sedimentary processes involve a wide variety of complex geochemistry and mineralogy that have varied considerably over both space and time. Such an emerging picture perhaps should not be surprising, given that the terrestrial sedimentary cycle, although differing greatly in detail, also exhibits considerable variability in both space and time.

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