

SULFUR AND THE SULFUR CYCLE ON MARS. Scott M. McLennan¹ and John P. Grotzinger², ¹Dept. of Geosciences, SUNY at Stony Brook, Stony Brook, NY, 11794-2100, USA (Scott.McLennan@sunysb.edu), ²Div. Of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, 91125, USA (grotz@gps.caltech.edu).

Introduction: Recent exploration of Mars has revealed remarkable new insights but the nature and history of surficial processes remain important unresolved questions. Sulfur-rich surface soil and dust deposits, recognition of ancient sedimentary sulfate deposits and apparent dearth of carbonates suggest that the S-cycle, characterized by low pH, rather than the C-cycle has dominated surficial processes during formation of much of the Martian geological record [1,2].

Critical issues in understanding any elemental cycle are the distribution and sizes of reservoirs and fluxes involved in elemental cycling. However, there is a general lack of quantitative understanding of global sulfur distributions on Mars. Accordingly, the purpose of this work is to better constrain both the size and distribution of sulfur reservoirs on Mars and begin to characterize the various pathways (processes) that may be involved in any near-surface Martian S-cycle.

Sulfur Reservoirs on Mars: The sulfur contents of rocky planets, their mantles and crusts are difficult to estimate, but Mars commonly is thought to be “S-rich” with primitive mantle compositions as much as 2X those of Earth (>400 ppm). Similarly, the composition of the Martian basaltic crust is also difficult to estimate but SNC meteorite data are consistent with a value of ~2,000 ppm, about twice that of terrestrial oceanic crust.

How much of that S has found its way into the sedimentary environment? Sulfur contents in martian sedimentary rocks and soils from Viking, Pathfinder and MER, combined with global mapping of the upper 0.5-1.0 m with Odyssey GRS, provides compelling evidence that sulfur is enriched in surficial deposits and many ancient sedimentary materials [2,3]. However, there is little understanding of the mass and distribution of these deposits in space and time and thus no way to directly estimate average sulfur content.

An alternative, though model-dependent approach is to estimate the mass of the sedimentary sulfur reservoir by modeling planetary degassing. Canfield [4] estimated that ~11% of the terrestrial primitive mantle sulfur had outgassed over geological time. On Earth, this cannot be equated to the present-day sedimentary sulfur reservoir because plate tectonics results in complex crust-mantle recycling. However, on Mars where plate tectonics was never established, it is plausible to assume that outgassed sulfur remained largely in the sedimentary realm. Thus, assuming the same degree

of degassing as the Earth and taking into account the S-rich nature of Martian crust and mantle leads to an estimate of 2.3×10^{22} g of S in the sedimentary reservoir. This is likely a lower limit since the crust/mantle system of Mars appears to be significantly more differentiated than the Earth [3]. For scale, this is equivalent to a planetary-wide 2km thick sedimentary layer with S content equal to average soil (~6% SO_3).

Early Martian Sulfur Cycle: Most volcanic activity, the ultimate source of sulfur at the martian surface, took place early in Martian history (>3 Gyr). This was also a time when relatively widespread aqueous conditions prevailed, possibly facilitated by an early greenhouse effect. Experimental and modeling studies and *in situ* measurements of mineralogical/chemical compositions of Martian rocks and soils have combined to identify a variety of processes involved in the surficial S-cycle (see ref. [2] for review). These are summarized in Fig. 1.

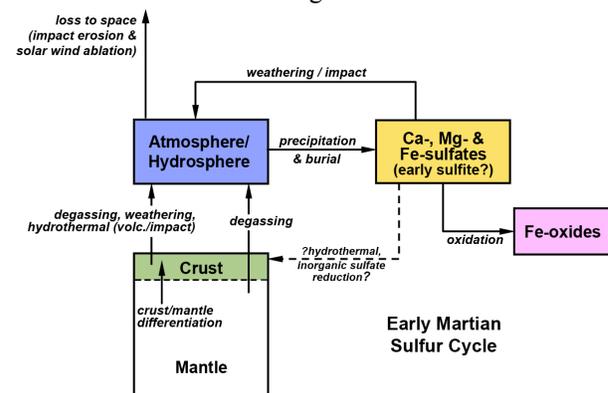


Fig. 1. Flow diagram showing major sulfur reservoirs, pathways and mechanisms during the early history (Noachian–(?)early Hesperian) of Mars. Dashed arrows are not well established recycling processes.

Weathering and hydrothermal alteration. Sulfuric acid alteration of basaltic rocks and minerals is well established on the Martian surface. Processes likely include both low temperature alteration, such as that required to produce high ionic strength fluids responsible for evaporitic minerals at Meridiani Planum, 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.

Evaporation. The widespread occurrence of sulfate and chloride minerals on the Martian surface observed

from orbit 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.

Oxidation. Correlations between occurrences of sulfates and iron oxides on the Martian surface, identified from orbit [5] suggest a genetic link. Evaporite-modeling of Martian brines predict the occurrence of ferrous (\pm ferric) sulfates. Ferric sulfates (e.g., jarosite) have been observed but ferrous sulfates have not. Accordingly Tosca et al. [6] experimentally evaluated diagenetic oxidation of iron sulfates leading to iron-oxides (Fig. 2). This is an irreversible process, liberating sulfur to be recycled back into the surficial environment and is likely to take place at rates largely governed by the availability of aqueous fluids.

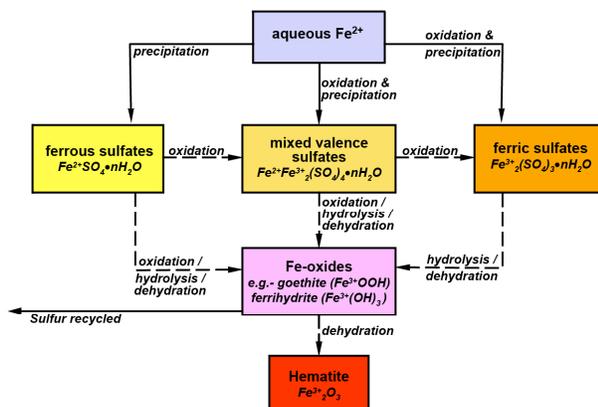


Fig. 2. Pathways of oxidation of ferrous sulfates to ferric sulfates and iron-oxides (after Tosca et al. [6]). Solid arrow represent deposition; dashed lines represent diagenetic alteration. Note that this is effectively an irreversible process.

Dissolution and Recycling. The terrestrial sedimentary record is strongly influenced by cannibalistic recycling processes and it is likely that recycling also influences the Martian S-cycle. Sulfur recycling during iron sulfate oxidation was discussed above. In addition, Mg- and Fe-sulfates are highly soluble and interaction with any dilute fluid is likely to result in weathering, dissolution and redistribution of sulfur. Impacts into sulfate deposits also have the potential to break down sulfate minerals and redistribute sulfur, analogous to that suggested for the late Cretaceous Chicxulub impact on Earth.

Present-day Martian Sulfur Cycle: There is clear evidence that the sulfur cycle continued beyond the time that volcanic and aqueous activity on Mars subsided. For example, rock surfaces analyzed by Spirit in Gusev crater show clear evidence of acid alteration in spite of being continually physically

abraded by eolian processes [7]. Thus, later in Martian geological history, it is likely that the S-cycle was dominated by recycling processes (e.g., impact, local dissolution) with minor additions from volcanic sources (Fig. 3), and proceeded at greatly diminished rates.

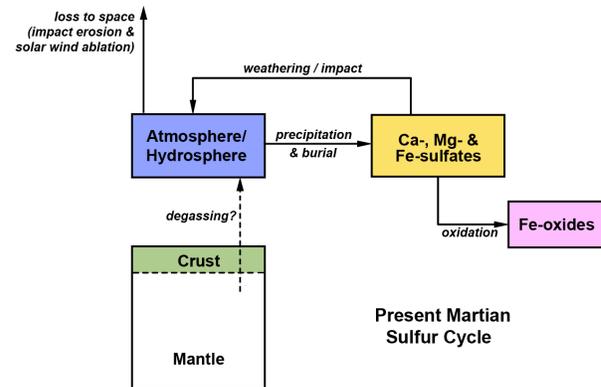


Fig 3. . Flow diagram showing major reservoirs and sulfur pathways and mechanisms during later, volcanically quiescent, drier periods of Martian history.

Discussion: In most respects the Martian S-cycle more closely resembles the terrestrial C-cycle (e.g., long-term and short-term cycles) rather than the terrestrial S-cycle, that currently is strongly influenced by biological processes and plate tectonic recycling (e.g., ref. [4]). The “long-term” part of the S-cycle, early in Martian history, resulted in storage of sulfur in the sedimentary record thus resembling the long-term C-cycle on Earth where the bulk of C is stored as carbonate rocks and C_{org} -rich sedimentary rocks. During later times, recycling of sulfur by various processes, such as impacts, dissolution/precipitation and Fe-sulfate oxidation, perhaps supplemented by limited sulfur outgassing from younger volcanism, provided minor amounts of acidic fluids resulting in highly water-limited acid alteration, such as that observed on present-day rock surfaces.

References: [1] Halevy, I. et al. (2007) *Science*, 318, 1903-1907. [2] McLennan, S. M. & Grotzinger, J. P. (2008) in J. F. Bell (ed.) *The Martian Surface: Composition, Mineralogy and Physical Properties*. Cambridge, 541-577. [3] Taylor, S. R. & McLennan, S. M. (2009) *Planetary Crusts: Their Composition, Origin and Evolution*, Cambridge. [4] Canfield, D. E. (2004) *Am. J. Sci*, 304, 839-861. [5] Bibring, J. P. et al. (2007) *Science*, 317, 1206-1210. [6] Tosca, N. J. et al. (2008) *JGR*, 113, E05005. [7] Hurowitz, J. A. & McLennan, S. M. (2007) *EPSL*, 260, 432-443.