Missing salts on early Mars

R. E. Milliken,[1] W. W. Fischer,[2] and J. A. Hurowitz[1]

[1]   Our understanding of the role of water on Mars has been profoundly influenced over the past several years by the detection of widespread aqueous alteration minerals. Clay minerals are found throughout ancient Noachian terrains and sulfate salts are abundant in younger Hesperian terrains, but these phases are rarely found together in the early Martian rock record. Full alteration assemblages are generally not recognized at local scales, hindering our ability to close mass balance in the ancient crust. Here we demonstrate the dissolution of basalt and subsequent formation of smectite results in an excess of cations that should reside with anions such as OH^-, Cl^-, SO_3^{2-}, SO_4^{2-}, or CO_3^{2-} in a significant reservoir of complementary salts. Such salts are largely absent from Noachian terrains, yet the composition and/or fate of these 'missing salts' is critical to understanding the oxidation state and primary atmospheric volatile involved in crustal weathering on early Mars. **Citation:** Milliken, R. E., W. W. Fischer, and J. A. Hurowitz (2009), Missing salts on early Mars, *Geophys. Res. Lett.*, *36*, L11202, doi:10.1029/2009GL038558.

1.   Introduction

[2]   Minerals formed during aqueous alteration of the crust and preserved in the sedimentary record provide important clues about the atmospheric composition, oxidation state, and geochemistry of early Mars. The most recent results of the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) on NASA's Mars Reconnaissance Orbiter (MRO) have confirmed previous detections of clay and sulfate minerals and revealed a greater diversity in their compositions [e.g., *Mustard et al.*, 2008]. Smectites have been reported to exist throughout the ancient Noachian crust and appear as the most conspicuous alteration product during that time [*Bibring et al.*, 2006; *Mustard et al.*, 2008]. In contrast, aqueous alteration products in younger Hesperian terrains are dominated by Mg/Fe-sulfates, ferric oxides, and opal [*Bibring et al.*, 2006, 2007; *Milliken et al.*, 2008; *Gendrin et al.*, 2005; S. L. Murchie et al., A synthesis of Martian aqueous mineralogy after one year of observations from the Mars Reconnaissance Orbiter, submitted to *Journal of Geophysical Research*, 2009]. This temporal-spatial variation in low temperature alteration minerals has been used to suggest that Mars experienced a major global environmental transition from neutral-alkaline to acidic aqueous conditions [*Bibring et al.*, 2006]. In this scenario, clay minerals such as smectites were the primary alteration product during the first ~1 Gyr on Mars, formed by the aqueous alteration of materials largely basaltic in composition [*Bibring et al.*, 2006; *Chevrier et al.*, 2007]. The hypothesis that the environmental history of Mars is captured in the chemistry of alteration minerals is potentially powerful. This approach, however, is currently hindered by our lack of understanding of the full secondary mineral assemblage occurring coeval with Noachian clay-bearing strata. Here we investigate the mass balance between chemical weathering of basalt and precipitation of alteration minerals known to reside in the ancient sedimentary record of Mars. As we demonstrate below, the chemical weathering of basaltic crust and subsequent formation of clays (smectites) yields an appreciable excess of cations that must reside in additional coeval alteration products, most likely in the form of sedimentary salts.

2.   Methods

[3]   Chemical weathering of basalt releases cations and silica into solution, the rate of which depends on the rate of dissolution of different primary mineral phases. The behavior of this process is captured by the model mineral dissolution curves shown in Figure 1a. These curves were constructed from the relationship in equation (1), which is commonly used in laboratory experiments to calculate mineral dissolution rates in a continuously-stirred tank reactor.

$$R = Q\frac{(C_o - C_i)}{(A_s m_i)} \qquad (1)$$

Here, R is the mineral dissolution rate in mol·cm^{-2}·s^{-1}, Q is the flow rate in L/s, C_o is the output concentration in mol/L, C_i is the input concentration in mol/L, A_s is the surface area in cm^2/g, and m_i is the mass of mineral in g. The following assumed values were used in the calculation: $Q = 10^{-6}$ L/s, $C_i = 0$ mol/L, $A_s = 100$ cm^2/g, total rock mass = 1000 g. We approximate the composition of the Martian crust using the modal mineralogy of average Adirondack class basalts from *McSween et al.* [2004]. Mineral dissolution rate constants at pH = 6 were then taken from the literature and input for R in equation (1). Rates for igneous fluorapatite were acquired from *Guidry and Mackenzie* [2003], forsteritic olivine (Fo$_{90}$) from *Pokrovsky and Schott* [2000], magnetite (TAH magnetite) and ilmenite from *White et al.* [1994], labradorite from *Blum and Stillings* [1995], enstatite from *Brantley and Chen* [1995], and diopside from *Chen and Brantley* [1998]. Equation (1) was arranged to solve for C_o and then recalculated in terms of moles of each mineral remaining for a given water-to-rock ratio and elapsed time.

[4]   Coupled to the basalt mineral dissolution calculations, we apportion the dissolved constituents into smectite clays (Figure 1), which have been detected throughout the Noachian crust [*Poulet et al.*, 2005; *Mustard et al.*, 2008]. We

[1]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, USA.
[2]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California, USA.
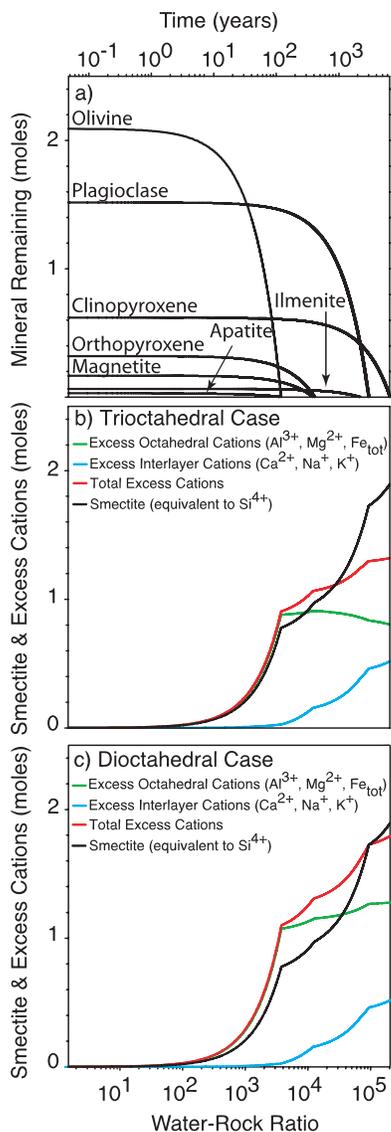
Figure 1. Chemical weathering of Martian basalt and excess cations produced by precipitation of smectite. (a) Modeled dissolution of igneous minerals in a Martian basalt and (b) predicted excess of cations formed along with trioctahedral clay (e.g., saponite) and (c) dioctahedral clay (e.g., nontronite, montmorillonite). Co-precipitation of additional silica-rich phases (e.g., opal) would result in even greater abundances of excess cations. Note that the amount of excess cations is larger than or equal to the moles of smectite formed for a wide range of water-to-rock ratios, thus significant amounts of complementary salts are expected to reside in the Martian crust.

assume that all silica entering solution is consumed to form smectite (i.e., Si behaves as a completely conservative element). Although silica often enters additional low temperature mineral phases in natural settings, including SiO_2 [*Heany et al.*, 1994; *Milliken et al.*, 2008], due to the elemental stoichiometry for smectite formation (discussed below), this relationship allows us to calculate the minimum amount of excess cations, and thus "excess salt", that would form as a result of the conversion of silica from basalt to smectite.

[5] The calculation of excess cations is performed by assuming an idealized smectite formula of $(M_{int})_{0.3}(M_{oct})_{2-3}Si_4O_{10}(OH)_2$, where M_{int} refers to interlayer cations and M_{oct} refers to octahedral cations, where the latter is two or three depending on whether dioctahedral or trioctahedral smectite is formed, respectively. For simplicity, we assume that Ca^{2+}, Na^+, and K^+ act as interlayer cations and Mg^+, $Fe^{2+,3+}$, and Al^{3+} act as octahedral cations; we make no assumption regarding the charge (oxidation state) of Fe. In the case of trioctahedral smectite (e.g., saponite), we apportion 3 cations (2 for dioctahedral smectites such as nontronite) from the octahedral cation pool and 0.3 cations from the interlayer cation pool to smectite for every 4 tetrahedral silicons in solution. The remaining cations in each of the two pools are then summed to produce the total number of moles of "excess cations" at each time step for comparison to the amount of smectite formed (Figure 1).

[6] The absolute moles of mineral remaining at a given water-to-rock ratio is dependent on input values for surface area, flow-rate, rock mass, and solution pH. However, the distribution of the dissolution curves relative to each other depends primarily on the relative dissolution rates of the minerals. Furthermore, mass balance and stoichiometry dictate that processes resulting in the conversion of any amount of basalt to smectite (whether by precipitation, transformation, or hydrothermal alteration) will yield excess cations, regardless of factors that may otherwise affect weathering rates.

3. Discussion

[7] The relationships in Figures 1a and 1b illustrate that the chemical weathering of Mars' basaltic crust and subsequent precipitation of smectites leaves behind a substantial amount of cations in solution, often in amounts greater or equal to the number of moles of smectite. Because of charge balance, these cations will ultimately have their sink in a complementary salt (e.g., carbonates, sulfates, chlorides), and the anions found in these salts will reflect the major volatile in the atmosphere and Brønsted acid (proton donor) in the weathering environment.

[8] Many recent remote sensing studies of Mars have focused on the discovery of clay minerals, and these detections are becoming ever more common in the Noachian-age crust [*Poulet et al.*, 2005; *Bibring et al.*, 2006; *Ehlmann et al.*, 2008a; *Michalski and Noe Dobrea*, 2007; *Grant et al.*, 2008; *Mustard et al.*, 2008]. However, less attention has been directed at uncovering additional secondary mineral phases and full alteration assemblages in order to meet mass balance constraints. It has been suggested that opaline silica may be associated with smectites in the Mawrth Vallis region [*Bishop et al.*, 2008]. If both formed *in situ*, then the precipitation of a pure silica phase would result in an even greater abundance of excess cations and missing salts than estimated in Figure 1. On a broader scale, although sulfate salts are common in younger Hesperian terrains [*Gendrin et al.*, 2005; *Bibring et al.*, 2006], localized outcrops of chloride salts [*Osterloo et al.*, 2008] and carbonates [*Ehlmann et al.*, 2008b] are exposed at the surface, and carbonates have been proposed to reside in the global dust at several volume percent [*Bandfield et al.*, 2003], these phases are significantly underrepresented in

Noachian terrains relative to abundant smectite deposits. The presence of thousands of clay outcrops in the ancient crust [*Mustard et al.*, 2008] imply that the excess cations reside with complementary anions such as OH^-, Cl^-, SO_3^{2-}, SO_4^{2-}, or CO_3^{2-} in a significant reservoir of coeval mineral salts. Identifying full mineral assemblages and discovering the location or fate of these "missing salts" in the Noachian rock record is the key to understanding environmental conditions on early Mars.

[9] A major lingering question about Mars' early environmental history comes from the need to explain ever growing geomorphological and sedimentological evidence for liquid water on the surface of the planet [e.g., *Carr*, 1996; *Grotzinger et al.*, 2006], particularly given the hypothesis of a fainter young sun. What was the major chemical species in the atmosphere responsible for greenhouse forcing and did this species participate in a climate-weathering feedback [e.g., *Walker et al.*, 1981]? The hypothesis of a Martian SO_2 rather than an Earth-like CO_2 climate-weathering feedback cycle [*Halevy et al.*, 2007] requires that sulfite minerals would have been present on early Mars, yet sulfites have not been detected on the surface. Rather, the most common salts detected in Martian sedimentary deposits have sulfate as the complementary anion, and these salts are rarely found to occur with smectites in rocks that are clearly Noachian in age [*Bibring et al.*, 2006; Murchie et al., submitted manuscript, 2009]. Though we stand to learn much from the discovery of Mars' missing salts, the identity of the complementary salt(s) we predict for the Noachian sedimentary record remains unknown. This discordance may result from inadequate means of detection using current orbital techniques, lack of preservation in the Noachian rock record, and/or spatial segregation and subsequent burial by younger strata. The positive identification of clays, the expected relative abundance of complementary salts (e.g., Figure 1), and the detection of sulfates, carbonates and other salts in post-Noachian strata [*Osterloo et al.*, 2008; *Ehlmann et al.*, 2008b; *Bibring et al.*, 2006] suggest detection limits alone cannot account for this absence in the ancient Martian rock record.

[10] It is possible that some of these 'missing salts' are not preserved in the ancient rock record due to later dissolution or separation through physical transport processes. The conspicuous Hesperian sulfate minerals, for instance, may have originally formed coeval with clays only to be subsequently dissolved, transported, and reprecipitated in the younger terrains in which they are now found. However, clay minerals would also be susceptible to these effects, especially if such fluids were acidic, and their preservation in the ancient crust and paucity in younger terrains suggests post-depositional leaching and/or subsequent large-scale sediment transport processes were not significant enough to erase their signature. Alternatively, the Earth's fluvial systems and oceans are effective agents of physical and chemical segregation of weathering products such as clays and carbonates, and similar processes may have occurred on early Mars. Although valley networks are widespread in Noachian terrains [*Carr*, 1996; *Fasset and Head*, 2008], the full extent of such segregation and the presence of a large chemical sink in the form of a northern ocean during the Noachian epoch remain unclear.

[11] The presence of clay-bearing units in the Eberswalde Crater delta provides an interesting example of the enigmatic 'missing salts'. The western portion of the crater contains a fossil delta that developed from aqueous transport of sediment to a body of water [*Malin and Edgett*, 2003], consistent with the topography that also suggests the crater is a closed basin. CRISM spectra exhibit weak but resolvable signatures indicative of clay minerals in the lower strata (bottomsets) of the delta (Figure 2), similar to terrestrial deltas. Clay minerals are also present in large blocky deposits, possibly ejecta from adjacent Holden Crater, located east of the current delta front. Additional non-clay alteration products have not yet been discovered in this closed basin. Given that water was present in the crater long enough for the delta to develop stratal geometries, indicating changes in base level [*Pondrelli et al.*, 2008; *Lewis and Aharonson*, 2006], it is likely that much of the water evaporated as opposed to infiltrating the subsurface. Therefore, though the clays in Eberswalde may be detrital and not indicative of local solution chemistry, the lack of chemical precipitates such as sulfates, chloride salts, or carbonates in this sedimentary basin is at odds with the evidence for the sustained presence and likely evaporation of a body of water. Like much of ancient Mars, the full alteration assemblage expected in this depositional environment has yet to be identified.

4. Conclusions

[12] Similar to Earth, local and regional environmental conditions on early Mars were likely highly variable. Mars' rock record is expected to preserve evidence for a range of pH levels, water activities, and oxidation states. The assemblage of mineral salts preserved at Meridiani Planum implies environmental conditions that were arid, acidic, and oxidizing, with a water activity too low to support terrestrial life [*Tosca et al.*, 2008]. In contrast, the identification of thick sedimentary deposits elsewhere on Mars that contain Fe-rich clays such as nontronite, which form under moderate pH and potentially reducing conditions [*Harder*, 1978], points to very different and perhaps more habitable conditions (Figure 3). The links between clay minerals, preservation of organic material, and habitability have made clay-bearing strata a prime target for the 2011 Mars Science Laboratory rover. However, many of the Martian clay deposits have yet to be considered in the context of full alteration assemblages based on geochemical constraints.

[13] We have demonstrated that dissolution of basalt and precipitation of smectites results in an excess of cations expected to reside in a complementary salt. The unknown host of these cations (e.g., carbonates, sulfates, hydroxides, etc.) presents an interesting gap in our understanding of low temperature alteration processes operating on early Mars. The lack of large-scale carbonate rocks associated with clay deposits has remained a puzzle, especially given the present-day CO_2 atmosphere of Mars and mildly alkaline pH levels in the Noachian required for smectite formation, conditions seemingly favorable to carbonate formation. Thermodynamic models [*Chevrier et al.*, 2007] and the potential for an early SO_2 feedback cycle [*Halevy et al.*, 2007] have been invoked to explain this discordance, but such models must be reconciled with mineral assemblages
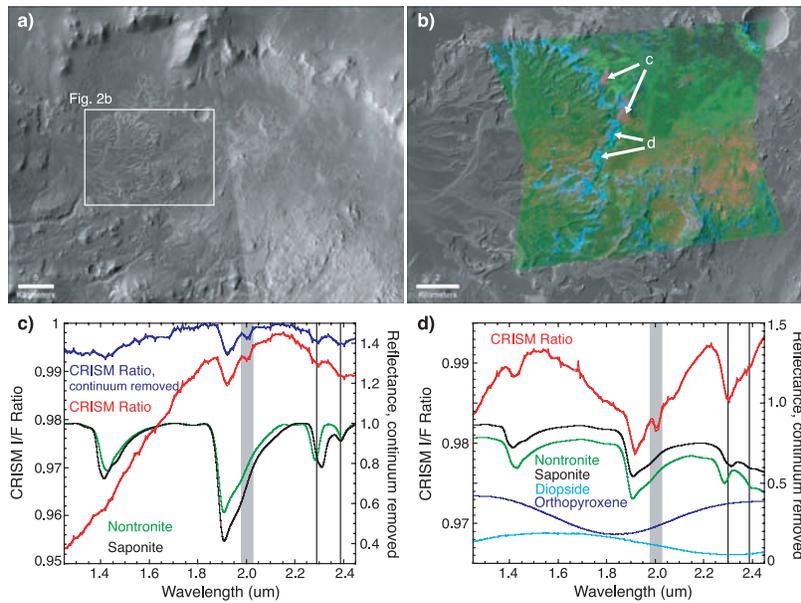
Figure 2. CRISM detection of clay minerals in Eberswalde crater. (a) MRO Context Camera mosaic of the delta. (b) CRISM RGB map of the ferrous band (red), pyroxene band (green) and 2.3 μm band depth (blue), where blue and magenta tones indicate clay minerals. CRISM I/F ratios corresponding to (c) the lower clay-bearing strata of the delta and (d) blocky material to the east of the delta front are consistent with the presence of clays. Hydrated sulfates or other salts have not yet been identified in this closed basin. CRISM radiance data were divided by the solar flux to convert to units of I/F, photometrically corrected by dividing the I/F values by the cosine of the incidence angle, and corrected for atmospheric gases using a scaled atmospheric transmission spectrum acquired over Olympus Mons [e.g., *Mustard et al.*, 2008]. The spectra shown here represent the ratios of spectra averaged over several hundred pixels corresponding to the clay-rich units in Figure 2b to a spectral average of several hundred pixels of a dusty, spectrally 'neutral' unit. Gray bars in spectral plots indicate areas of incomplete atmospheric removal.
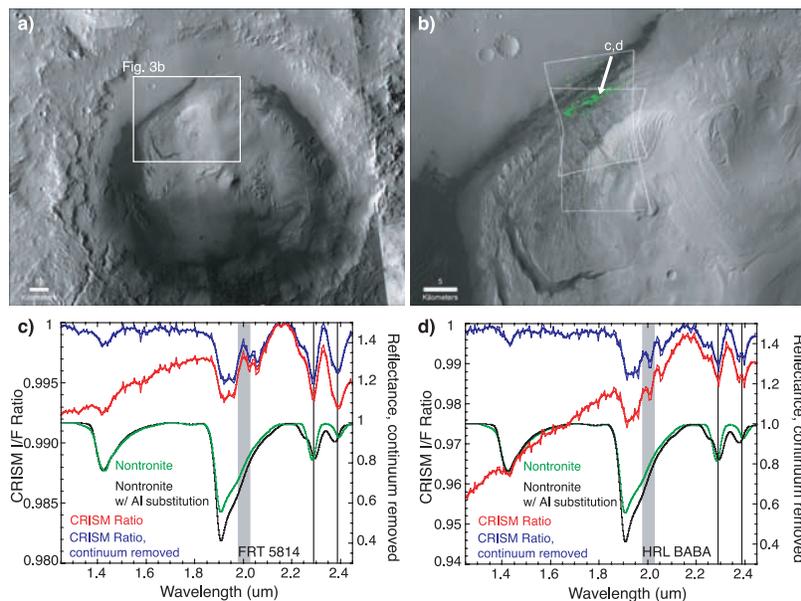

Figure 3. CRISM detection of Fe-rich smectite in Gale Crater. (a) MRO Context Camera mosaic of thick sedimentary sequences in Gale Crater for which (b) CRISM maps of the 2.3 μm band depth (green) exhibit evidence for clay minerals; white outlines represent CRISM images. (c and d) CRISM I/F ratio spectra of the same region from two different observations reveal that the position of the metal-OH absorption near 2.29 μm is most consistent with the Fe-rich clay nontronite (opposed to an Mg-rich saponite), which can form at moderate pH under reducing conditions [*Harder*, 1978]. CRISM data and ratio spectra were analyzed using the same techniques described for Figure 2. Gray bars in spectral plots indicate areas of incomplete atmospheric removal.

and processes recorded in the stratigraphic record. Determining the composition or fate of the elusive, complementary salts in the Noachian rock record is ultimately necessary to identify the oxidation state of the early atmosphere and the primary atmospheric volatile involved in crustal weathering, and it is this knowledge that will allow us to assess the potential operation of a geochemical climate-weathering feedback capable of sustaining long-term clement conditions on early Mars.

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W. W. Fischer, Division of Geological and Planetary Sciences, California Institute of Technology, 1200 East California Boulevard, Pasadena, CA 91125, USA.

J. A. Hurowitz and R. E. Milliken, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA. (ralph.milliken@jpl.nasa.gov)