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A ~3.5 Ga record of water-limited, acidic weathering conditions on Mars

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Abstract

The secondary mineral budget on Earth is dominated by clay minerals, Al-hydroxides, and Fe-oxides, which are formed under the moderate pH, high water-to-rock ratio conditions typical of Earth's near-surface environment. In contrast, geochemical analyses of rocks and soils from landed missions to Mars indicate that secondary mineralogy is dominated by Mg (±Fe, Ca)-sulfates and Fe-oxides. This discrepancy can be explained as resulting from differences in the chemical weathering environment of Earth and Mars. We suggest that chemical weathering processes on Mars are dominated by: (1) a low-pH, sulfuric acid-rich environment in which the stoichiometric dissolution of labile mineral phases such as olivine and apatite (±Fe–Ti oxides) is promoted; and (2) relatively low water-to-rock ratio, such that other silicate phases with slower dissolution rates (e.g., plagioclase, pyroxene) do not contribute substantially to the secondary mineral budget at the Martian surface. Under these conditions, Al-mobilization is limited, and the formation of significant Al-bearing secondary phases (e.g., clays, Al-hydroxides, Al-sulfates) is inhibited. The antiquity of rock samples analyzed *in-situ* on Mars suggest that water-limited acidic weathering conditions have more than likely been the defining characteristic of the Martian aqueous environment for billions of years.

Keywords: Mars; weathering; rates; aluminum; clay; APXS

1. Introduction

On the basis of *in-situ* chemical analyses of rocks and soils on Mars, it is becoming increasingly clear that chemical alteration on Mars proceeds under a different set of conditions than they typically do on Earth. On Earth, chemical analyses for rocks weathered under a wide range of environmental conditions indicate that, regardless of the type of rock (e.g., granite, andesite, and basalt), the results of chemical alteration are broadly similar. Primary igneous rocks are stripped of soluble cations, resulting in residual enrichment in aluminum and total iron (dominantly as ferric iron). This process promotes the formation of large quantities of clay minerals and iron-oxides. In contrast, Mars does not appear to possess an environment in which the generation of a similar suite of secondary minerals is a globally important process. Instead, Martian secondary mineralogy is dominated by Mg (±Fe, Ca)-sulfates and

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Fe-oxides. Here, we present evidence that these differences in bulk secondary mineralogy are primarily due to the fact that chemical weathering processes on Mars occur at low-pH, and are typically incipient in nature, thus implying low water-to-rock ratios. As on Earth, data collected from chemically weathered materials allows one to make inferences regarding the environmental conditions under which alteration took place. Accordingly, we will discuss the implications of data from chemically altered Martian materials for the global Martian environment.

2. Data sources and sample collection site conditions

Data for the major element chemistry of igneous rocks weathered in the terrestrial environment were taken from the studies of Moon and Jayawardane (2004), Morris et al. (2000), Nesbitt and Wilson (1992), Nesbitt and Markovics (1997), Patino et al. (2003), and Sak et al. (2004). These data include granodioritic, andesitic, and basaltic compositions of varying crystallinity. Weathering conditions in the above referenced studies span a range of mean annual temperature from 2 to 28.7 °C, and mean annual precipitation from 175 to 3085 mm H_2O. The sampling scale in the above referenced studies, from unaltered igneous protolith to weathered materials, ranges from centimeters to meters. Data for the major element chemistry of terrestrial river waters was taken from Meybeck (2003), and represent rivers draining various plutonic and volcanic terranes ranging in composition from granitic to peridotitic. For the river water chemistry reported in Meybeck (2003), only elemental data for Mg, Ca, Na and K are provided, likely owing to the exceedingly low concentrations of dissolved Fe and Al in most terrestrial river waters.

Data for the major element chemistry of Martian samples are taken from Clark et al. (1982) for soils from the Viking 1 landing site at Chryse Planitia, Foley et al. (2003) for rocks and soils from the Pathfinder landing site at Ares Vallis, Gellert et al. (2006) for rocks and soils at the Mars Exploration Rover (MER) Spirit landing site in Gusev Crater, Rieder et al. (2004) for rocks and soils at the MER Opportunity landing site at Meridiani Planum, and Gellert and Rieder (2006) for rocks and soils at both MER landing sites. These data have been obtained by remote analysis using variations on the X-ray fluorescence technique to obtain bulk chemical analyses of Martian rocks and soils; the reader is referred to Rieder et al. (2003, 1997) and Toulmin et al. (1973) for details of the methodologies. Martian samples include igneous rock interiors that have experienced variable degrees of chemical alteration, rock alteration rinds, dust/soil covered rock surfaces, soils, and evaporite-cemented sandstones. Currently, Mars' climate is exceedingly cold and dry, with an annual global average temperature of −50 °C, a total atmospheric pressure of 6 millibars, and only 10^{-3} mbars of H_2O (Jakosky and Phillips, 2001). In the past, conditions on Mars may have been significantly different than they are at present, but the notion of a "warmer and wetter" Mars remains controversial.

3. Discussion

3.1. Major element chemistry of weathered rocks on Earth

On Fig. 1A, a ternary diagram which plots the molar proportions of Al_2O_3, $(CaO+Na_2O+K_2O)$, and (FeO_T+MgO) at the apices, data for terrestrial igneous rocks and their weathering products are shown. Such diagrams have long proven useful for evaluating the changes in major element chemistry which take place as igneous rocks are chemically weathered on Earth [e.g., Nesbitt and Young, 1982, 1984; McLennan et al., 1993, 2002; Nesbitt, 2002]. Unweathered igneous rocks plot in the lower left hand portion of the diagram (below the dashed line) because the primary igneous minerals, including feldspar, pyroxene, olivine, and the Fe–Ti oxides, all plot in this region of the diagram. Variation in primary igneous composition is expressed as a linear trend subparallel to the feldspar — (FeO_T+MgO) join (dashed line on Fig. 1A), a result of the fact that felsic rocks tend to be relatively enriched in feldspar, whereas mafic rocks tend to be relatively enriched in olivine, pyroxene and Fe–Ti oxides.

Chemical alteration is expressed on Fig. 1A as a linear trend from unweathered igneous rock (below the dashed line) towards the Al_2O_3–(FeO_T+MgO) axis, as demonstrated by the arrow drawn through the Baynton basalt weathering profile (Nesbitt and Wilson, 1992). This alteration trend is roughly perpendicular to the trend of primary igneous variation. The chemical alteration trajectory demonstrated on Fig. 1A results from the insoluble nature of Al and Fe(III) relative to Mg, Ca, Na, and K at the moderate pH at which most water-to-rock reactions take place on Earth (Stumm and Morgan, 1996). In addition, Fe(II), which is a relatively soluble element, is rapidly oxidized to insoluble Fe(III) at the moderate pH values typical of terrestrial waters (Stumm and Morgan, 1996). Because water–rock interactions at moderate pH result in the removal of Mg, Ca, Na, and K from igneous rocks, natural waters become enriched in these elements, and river waters accordingly plot along

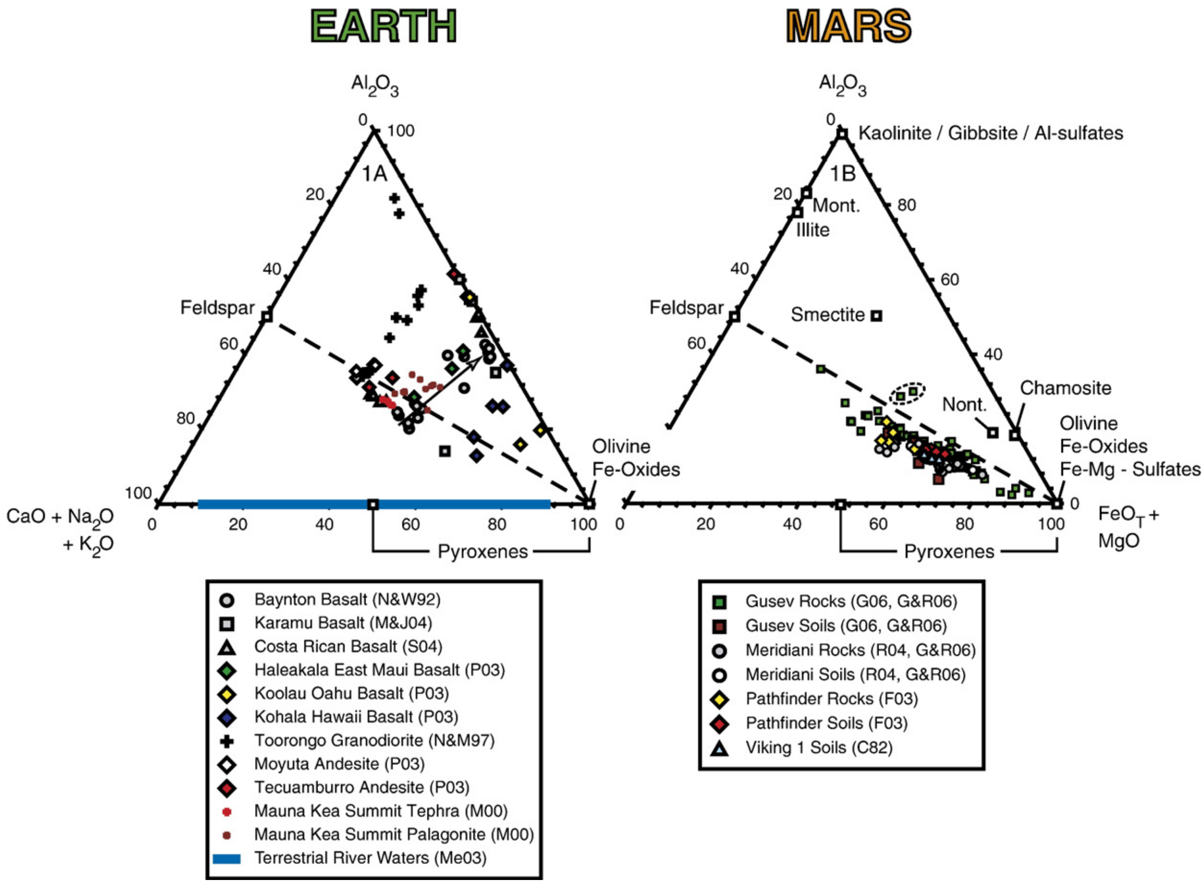

Fig. 1. A and B: Ternary Al_2O_3, $(CaO+Na_2O+K_2O)$, (FeO_T+MgO) diagrams, data plotted in mole percent. Fig. 1A shows data for weathered terrestrial igneous rocks, Fig. 1B shows data for Martian rocks and soils analyzed during the Viking 1, Pathfinder, and MER missions. Grey arrow on Fig. 1A indicates alteration trajectory for terrestrial weathering processes, drawn through the Baynton basalt weathering profile. Dashed ellipse on Fig. 1B denotes the samples Assemblee_Gruyere and Assemblee_APXS. Nont. = nontronite, Mont. = montmorillonite. Legend text enclosed in parentheses are abbreviations of first author's last name and publication year for study.

the $(CaO+Na_2O+K_2O)$–(FeO_T+MgO) axis on Fig. 1A. As these soluble elements are leached from the igneous protolith, the weathered residuum is enriched in Al and Fe (III), resulting in conditions that favor the precipitation of aluminous secondary minerals (e.g., clays, Al-hydroxides, etc.) and ferric iron oxides (e.g., goethite, hematite, etc.). For reference, a number of these secondary phases are shown on Fig. 1B.

As shown on Fig. 1A, the chemical composition of the unweathered protolith does not appear to affect the overall weathering trajectory. The bulk compositional effect of chemical alteration is broadly similar for the Toorongo granodiorite, the Fe–Mg-rich Koolau Oahu basalt, and all of the intermediate compositions on Fig. 1A. The sampling scale does not appear to have a dramatic effect on the major element chemical trends depicted on Fig. 1A either. As shown, the weathering trend is the same for the Costa Rican basalt and the Baynton basalt, whose sampling scales from unaltered protolith to weathered rock are on the order of centimeters and meters, respectively. Neither do the changes in chemical composition demonstrated on Fig. 1A appear to be strongly influenced by climate. As discussed above, the data on Fig. 1A span a large range in climatic conditions, yet the effect of chemical alteration is similar. More than likely, it is the rate at which primary igneous minerals are converted to secondary phases which is affected by differences in annual average temperature and precipitation on Earth.

This is not to say that the details of chemical weathering are exactly the same for each weathering profile plotted on Fig. 1A. It is well established that factors such as the saturation state of fluids with respect to the minerals undergoing alteration, physical weathering rates, the surface area of rock undergoing alteration, etc., will have a strong impact on the overall consequences of chemical weathering for individual profiles (Gislason and Arnorsson, 1993; White, 1995; Nesbitt, 2002). Rather, we point out that soluble element depletion, coupled to enrichment in insoluble Al and Fe (III), are dominant processes in determining the major element chemistry of weathered rock under terrestrial conditions, regardless of the initial composition of the protolith.

3.2. Major Element Chemistry of Weathered Rocks and Soils on Mars

In contrast to the data presented for weathered terrestrial rocks, Martian rocks and soils do not give much indication that chemical alteration processes on the Red Planet are readily comparable to those occurring in the terrestrial environment (Fig. 1B). There are only two samples plotted on Fig. 1B (analyses from Gusev Crater named Assemblee_Gruyere and Assemblee_APXS), which appear to have evolved towards an aluminous composition similar to those encountered in the terrestrial environment. Clark et al. (2007) have suggested that these two samples, in addition to three other analyses which together comprise the "Independence Class", have compositions consistent with the presence of montmorillonite, or a non-crystalline aluminosilicate (such as allophone) with a composition similar to montmorillonite.

For the vast majority of samples (representing 247 analyses), however, the variation amongst Martian samples appears to mimic primary igneous variation, expressing itself as scatter sub-parallel to the feldspar — (FeO_T+MgO) join. Represented within this dataset, however, are:

1. Secondary sulfate and iron-oxide rich soils sampled at both surface and subsurface locations;
2. Rock exteriors which are contaminated by soil, and which have been shown in many cases to possess surface alteration rinds; and
3. Sulfate-cemented sandstones of sedimentary origin.

In fact, given the high SO_3 (±Cl and Br) concentration of the interiors of nearly every rock of igneous origin analyzed on Mars, one could make the case that some chemical alteration process has taken place to affect the composition of all of the igneous rocks plotted on Fig. 1B as well. Only one *in-situ* rock analysis plotted on Fig. 1B, BounceRock_Case_RAT, has a SO_3 concentration lower than 0.75 wt.% (Gellert and Rieder, 2006), which is generally assumed to be the maximum plausible igneous SO_3 concentration for a Martian basaltic rock (McSween et al., 2004). Neither Mössbauer spectrometer on the MERs Spirit or Opportunity has identified Fe-sulfide minerals in the rocks analyzed by these rovers. The high SO_3 contents of these samples must therefore be predominantly associated with sulfate minerals, an assumption that has been verified by unambiguous sulfate mineral identifications using instruments such as the miniature thermal emission spectrometer and Mössbauer spectrometers onboard the Spirit and Opportunity rovers, and the OMEGA spectrometer onboard the Mars Express orbiter (Klingelhofer et al., 2004; Morris et al., 2004; Bibring et al., 2005; Glotch et al., 2006; Ruff et al., 2006). Given these multiple lines of evidence against pristine igneous compositions, it appears that some chemical alteration process is required in order to explain the data plotted on Fig. 1B. These marked differences in the elemental compositions of weathered rocks on Earth and Mars raises the question: what is different about chemical weathering processes on these two planets?

3.3. Weathering in acidic environments: examples from Mars and the laboratory

One significant difference between terrestrial and Martian alteration processes may be the pH at which water–rock interactions take place. It has long been suspected that low-pH conditions have been important in alteration processes in the near-surface environment on Mars (Clark et al., 1979; Settle, 1979; Burns, 1993). Unambiguous evidence for low-pH conditions on Mars has been provided by the Spirit and Opportunity rovers at Gusev Crater and Meridiani Planum, where both Mössbauer spectrometers have detected abundant ferric-sulfate minerals, including jarosite, in both rocks and soils (Klingelhofer et al., 2004; Morris et al., 2006). This important class of minerals forms exclusively at low-pH. Of global significance, the abundance of the nanophase Fe-oxide component of Mössbauer spectra in the fine, wind-blown dust at both landing sites correlates positively with SO_3 content, suggesting that ferric sulfate is also present in this globally distributed material (Yen et al., 2005).

Further insight into the style of chemical alteration on Mars can be gained by the examination of weathering rinds on igneous rocks at Gusev Crater. In every instance for which the interior composition of a rock can be compared with the composition of its' corresponding exterior surface, it has been demonstrated that there is an alteration rind present. In one case, for the rock “Mazatzal”, the rock surface appears to possess a relatively thick coating of secondary salt precipitates and Fe-oxides (McSween et al., 2004; Haskin et al., 2005). In all other cases, the difference in composition between the rock interior and exterior are consistent with a dissolution process that has stripped the rock surface of the elements contained in the mineral phase with the fastest laboratory-determined dissolution rate (Hurowitz et al., 2006).

As an example, the differences in chemical composition between the surface and interior of Adirondack Class basalts from Gusev Crater, shown on Fig. 2A, appear to result from the dissolution of olivine from the rock surface. The process leading to alteration rind formation on Adirondack Class basalts, and the resultant changes in rock surface chemistry, are well described by the experimental alteration of a synthetic Martian olivine-bearing basalt with a low-pH sulfuric acid-rich solution at low water-to-rock ratio (Tosca et al., 2004). As shown on Fig. 2B, experimental results indicate that because olivine is the most readily dissolved phase, the rock becomes depleted in the elements associated with olivine (i.e., FeO_T+MgO) as alteration proceeds. Accordingly, the fluid which altered the rock is enriched in the elements associated with olivine. Evaporation of this Fe- and Mg-rich fluid under low-pH conditions results in the formation of Fe- and Mg-sulfates and Fe-oxides (Tosca et al., 2004). Interestingly, comparison of the *in-situ* (Fig. 2A) and experimental (Fig. 2B) data to the total Martian dataset (Fig. 1B) indicates that the dissolution of olivine and the resulting precipitation of Fe–Mg sulfates and Fe-oxides may exert a significant control on the chemical composition of Martian soils and rocks.

This observation is in accord with evidence that olivine alteration plays a significant role in determining the chemical composition of soils at the MER landing sites in Gusev Crater and Meridiani Planum. Soils at both sites show a negative correlation between the Mössbauer determined amount of Fe associated with olivine and: (1) Fe associated with secondary nanophase ferric iron oxide, and (2) SO_3 content as determined by Alpha particle X-ray spectrometry (Klingelhofer et al., 2004; Yen et al., 2005; Gellert et al., 2006; Gellert and Rieder, 2006; Morris et al., 2006). By inference, soils from the Pathfinder and Viking landing sites might be expected to exhibit the same relationship given the

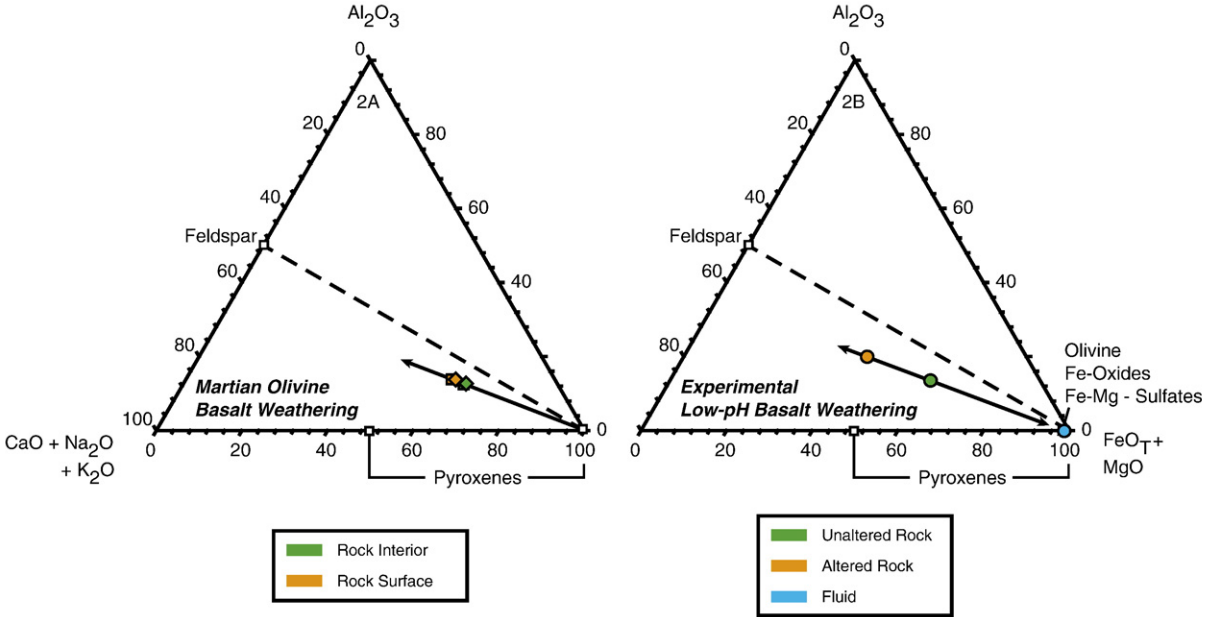

Fig. 2. A and B: Ternary Al_2O_3, (CaO+Na_2O+K_2O), (FeO_T+MgO) diagrams, data plotted in mole percent. Fig. 2A plots the chemical compositions of rock interior and rock surface analyses from the rocks Adirondack and Humphrey in Gusev Crater. The differences in chemical composition between these analyses are consistent with olivine dissolution from the rock surface. Note that the uncertainties on these analyses lie within the space occupied by the symbols, indicating these small offsets are real differences in chemical composition. Fig. 2B plots unaltered olivine-bearing basalt, and the products of its experimental alteration under low-pH, low water-to-rock ratio conditions. Alteration products are represented by the “altered rock”, and “fluid” datapoints. The dominant alteration process under these conditions is also olivine dissolution; note the similarity to the trend shown on Fig. 2A.

similarity of the chemical compositions of these soils to those analyzed at both MER landing sites.

The chemical composition of the evaporite component of sandstones examined by the Opportunity rover at Meridiani Planum also appears to be dominated by Mg- and Fe-sulfates and Fe-oxides, with lesser Ca-sulfate present as well. The chemical composition of the evaporitic cements could be readily generated by the dissolution of an olivine-rich basaltic substrate in a sulfuric acid-rich fluid, with subsequent evaporation and diagenesis resulting in the formation of sulfates and Fe-oxides, as well as significant amorphous silica (Tosca et al., 2005; Clark et al., 2005; McLennan et al., 2005; Glotch et al., 2006; Squyres et al., 2006a). A similar argument could plausibly be made for the sulfate component of the Peace Class outcrops examined by the *Spirit* rover at Gusev Crater, which appear to be evaporite cemented sandstones (Squyres et al., 2006b). These collective datasets, for weathering rinds on igneous rock surfaces at Gusev Crater, evaporitic materials from Meridiani Planum and Gusev Crater, and soils from globally separated landing sites, are consistent with the notion that the dissolution of olivine, and the precipitation of secondary Fe–Mg sulfates and Fe-oxides, is a globally important process on Mars.

It is important to note that while the above discussion emphasizes the importance of olivine alteration in controlling the chemical composition of secondary minerals on Mars, weathering processes are not selective for particular mineral phases. Undoubtedly, any acidic fluid that contacts a rock or soil will attack all of the mineral phases (or glass) present in the substrate. It is the fact that the dissolution rate of olivine is so much faster than that of the other materials present in basaltic rocks and soils that allows this mineral to exert such a strong influence on Martian alteration processes. As will be discussed in the next section, the fact that alteration also appears to proceed under water-limited, rock-dominated conditions allows olivine to further influence the chemical composition of secondary minerals on Mars.

3.4. Aluminum mobility and implications for water-to-rock ratio

Based on the relationships shown on Fig. 1A it is clear that variations in aluminum distribution play a major role in determining the chemical composition of weathered materials on Earth. As discussed previously, this is a result of the fact that Al is highly insoluble at moderate pH, resulting in the residual enrichment of Al in weathered rocks and the formation of abundant clay minerals and Al-hydroxides (e.g., gibbsite).

If, however, low-pH processes are important on Mars then one could reasonably expect Al to be a relatively *mobile* element during aqueous alteration of Martian rocks. This is because Al exhibits pH-dependent solubility such that Al concentration in solution can increase by orders of magnitude as pH decreases (Stumm and Morgan, 1996). Sulfuric acid-rich conditions would promote the formation of Al-sulfate minerals, which plot at the apex of the ternary diagram on Fig. 1B. The formation of Al-sulfate has been demonstrated experimentally during low-pH, sulfuric acid-rich alteration of olivine-poor basalts under Martian conditions (Banin et al., 1997; Golden et al., 2005; Hurowitz et al., 2005). On Earth, Al-sulfates are often found in association with acid-mine drainage settings when acidic fluids interact with the felsic rocks typical of the Earth's upper crust (Bigham and Nordstrom, 2000). The data plotted on Fig. 1B, however, give no indication that significant amounts of Al-sulfates have formed at the locations of landed missions to Mars. Neither do the data plotted on Fig. 1B provide much indication that clays or Al-hydroxides are an important component of the secondary mineral budget on Mars, though it would be more difficult to unambiguously rule out the influence of Fe-rich phyllosilicates such as nontronite or chamosite, which have recently been detected by the OMEGA spectrometer onboard the Mars Express Orbiter (Bibring et al., 2005; Poulet et al., 2005).

The most straightforward way to produce an Al-deficient assemblage of secondary minerals in an acidic environment is to maintain low water-to-rock ratio conditions, as illustrated on Fig. 3A, a plot of % mineral remaining against water-to-rock ratio. The modeled mineral dissolution curves on Fig. 3A were constructed utilizing the equation: $R = Q*(C_o - C_i)/(A_s*m_i)$, which is used in laboratory experiments to calculate mineral dissolution rates in a continuously-stirred tank reactor. In the equation, R = mineral dissolution rate in $\mathrm{mol \cdot cm^{-2} \cdot s^{-1}}$, Q = flow rate in L/s, C_o = output concentration in mol/L, C_i = input concentration in mol/L, A_s = surface area in $\mathrm{cm^2/g}$, and m_i = mass of mineral in g. The following assumed values were used in the calculation: $Q = 10^{-6}$ L/s, $C_i = 0$ mol/L, $A_s = 100\ \mathrm{cm^2/g}$, total rock mass = 1000 g. The modal mineralogy of average Adirondack class basalts from McSween et al. (2004) was used to partition the mass fraction of minerals in the basalt. Mineral dissolution rate (pH = 4) values were then taken from the literature and input for "R" in the equation. Rates for igneous fluorapatite were taken from Guidry and Mackenzie (2003), forsteritic olivine (Fo_{90}) from Pokrovsky and Schott (2000),

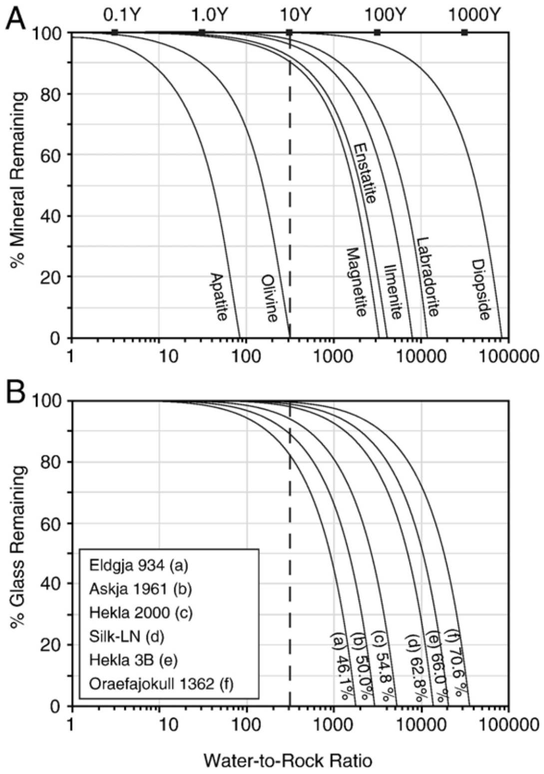

Fig. 3. A: Plot of % mineral remaining against water-to-rock ratio. Dashed line indicates the point in our calculation where olivine has been completely dissolved from the system (water–rock ratio ~300), note that ≤10% of the remaining phases have been dissolved at this point in the calculation. Mineral lifetimes are also shown along the top of the graph. See Section 3.4 for details of curve construction. B: Plot of % glass remaining against water-to-rock ratio. The names of the glass samples from Wolff-Boenisch et al. (2004) are shown in the legend, with the parenthetical lower-case letters indicating the corresponding glass dissolution curves. The SiO_2 content (weight %) of each glass is shown next to the corresponding glass dissolution curve. Dashed line indicates the point in our calculation where olivine has been completely dissolved from the system (see Fig. 3A), note that <20% of the lowest-silica glass has been dissolved at this point on Fig. 3. B. See Section 3.4 for details of curve construction.

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). The equation was then rearranged and solved for C_o, which was then recalculated in terms of percentage of each mineral remaining for a given water-to-rock ratio. We note that the value calculated for % mineral remaining at a given water-to-rock ratio is dependent on input values for surface area, flow-rate, rock mass, and pH. The distribution of the curves relative to each other, however, is dependent primarily on the relative dissolution rates of the minerals, though variation in relative surface areas of the minerals (e.g., in a phenocrystic rock sample) will have an effect on the distribution of the curves as well.

In Fig. 3A, the entire complement of apatite and olivine is dissolved out of the rock by the time water-to-rock ratio has reached a value of ~300. At this point, less than ~10% of the other minerals present in the rock have been dissolved, including plagioclase, the primary source of Al. On the basis of these relationships, we hypothesize that the lack of significant Al-bearing secondary mineral phases inferred from the relationships shown on Fig. 1B are the result of an alteration environment on Mars which is characterized by acidic, low water-to-rock ratio conditions that produce a system in which plagioclase dissolution does not make a significant contribution to the overall secondary mineral budget at the Martian surface. Such conditions appear to be prevalent at multiple scales on Mars, and are consistent with the processes that form thin alteration rinds at the surfaces of basaltic rocks at Gusev Crater, as well as the massive quantities of sulfate minerals present in the Meridiani Planum outcrop deposits. The primary characteristic of the alteration processes occurring at these localities is that, regardless of the total fluid volumes involved, alteration has occurred at low water to rock ratio.

Also shown on Fig. 3A, the lifetime of olivine for the conditions being simulated is approximately 10 years. If we assume a spherical particle shape for the olivine grains, then a particle diameter can be calculated with the equation $A_s=6/\rho d$ (Parks, 1990). In this calculation the number 6 is a “shape factor” for spherical particles, A_s=surface area (100 cm^2/g), and r=density (3.3 g/cm^3). Note that this surface area value is the same as that used in the construction of the curves on Fig. 3A. The value calculated for diameter (d) using this equation is 0.018 cm. Our ~10 year lifetime (Fig. 3A) for olivine is nearly identical to that calculated by Olsen and Rimstidt (2007) who calculate a ~10 year lifetime for a spherical forsteritic olivine grain with a particle dameter of ~0.02 cm dissolving in a pH 4 fluid.

A valid question to be raised with respect to Fig. 3A is where glasses might plot on this diagram? Basaltic glass dissolution at low-pH should be expected to release all cations in proportions approximately equal to their stoichiometric proportions in the glass, and thus might be expected to contribute considerable aluminum to solution. We have utilized the results of the glass dissolution rate experiments of Wolff-Boenisch et al. (2004) to construct a diagram similar to Fig. 3A showing the behavior of glasses of varying SiO_2 content. The modeled glass dissolution curves on Fig. 3B were constructed utilizing the same equation and input values for flow rate, surface area, and total mass as in Fig. 3A. Each glass dissolution curve assumes 1000g of glass, and rates have been normalized to the specific surface areas measured by Wolff-Boenisch et al. (2004) (rather than geometric surface area) in order to make direct comparison between Fig. 3A and B possible.

Wolff-Boenisch et al. (2004) demonstrated that dissolution rates for glasses are dependent on SiO_2 content, with silica-poor glasses dissolving more readily than silica-rich glasses. As shown on Fig. 3B, these experimental dissolution rates indicate a wide range of glass behavior, with the lowest-silica glass (Eldgja 934, 46.1 weight % SiO_2) completely dissolved at a water to rock ratio of ~2000, and the highest silica glass (Oraefajokull 1362, 70.6 wt.% SiO_2) dissolved at a water-to-rock ratio of ~40,000. Interestingly, these modeling results indicate that despite the fact that the low-silica Eldgja 934 basaltic glass dissolves at a relatively rapid rate, it still persists longer than does olivine in our calculation (Fig. 3A). Approximately 20% of the Eldgja 934 glass is predicted to have been removed at the water-to-rock ratio at which olivine has been completely removed. So it appears that glass, the other potential source of aluminum besides plagioclase, does not react as rapidly as does olivine. We therefore predict that basaltic glass dissolution is not a dominant contributor to the secondary mineral budget of the Martian surface either. If it were, then a larger complement of Al-bearing secondary phases would be expected in addition to Mg- and Fe-bearing phases.

3.5. Implications for long-term Martian climate

On Fig. 4, two geologic timescales are shown, showing the age of emplacement of the terrestrial and Martian rock samples discussed throughout this report. Terrestrial datasets represent the products of geologically recent weathering on Earth. With the exception of the Toorongo granodiorite, which is Devonian in age, the protoliths of all weathered samples plotted on Fig. 1A were emplaced during the Cenozoic (i.e., <65 Ma). Furthermore, the development of weathering profiles and weathering rinds in the terrestrial environment is known to occur on timescales as short as 10^3–10^6 years [e.g., Moon and Jayawardane, 2004; Sak et al., 2004]. The formation of extensively altered, Al-rich weathering products is, therefore, a relatively rapid process under terrestrial environmental conditions.

In contrast, weathered rocks analyzed on Mars represent processes affecting ancient materials. Meridiani chemical sediments have an estimated age of late

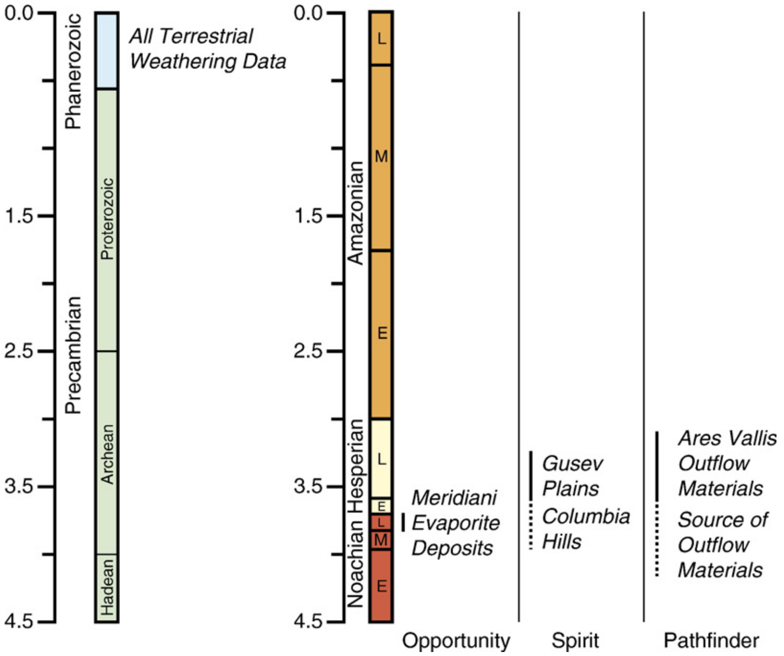

Fig. 4. Geologic timescales for Earth and Mars with rocks plotted at the age of their emplacement. The age of soil samples analyzed by landed missions to Mars are too uncertain to plot on Fig. 4, and since no rocks were analyzed at the Viking 1 landing site in Chryse Planitia, that site is not shown. Martian geologic timescale of Hartmann and Neukum (2001), with subdivisions indicating the early, middle, and late Noachian, early and late Hesperian, and early, middle, and late Amazonian.

Noachian (Arvidson et al., 2006a; Lane et al., 2003). The evaporitic component of the rocks must have been generated via the alteration of rocks which are even older than the Meridiani evaporites themselves. These rock samples therefore indicate that low-pH, water-limited alteration processes were occurring early in Martian geologic history.

For weathered igneous rock and soil samples from the Spirit, Pathfinder, and Viking landing sites, demonstrating the antiquity of low-pH, low water to rock ratio weathering processes is not so straightforward. Basaltic rocks analyzed by the Spirit rover on the plains of Gusev Crater are estimated to be ~3.5 Ga (early late Hesperian) in age, while the rocks analyzed by Spirit in the Columbia Hills of Gusev Crater are thought to be older than the plains on the basis of superposition relationships (Arvidson, et al., 2006b; Kuzmin et al., 2000; Greeley et al., 2005; Cabrol et al., 1998). Rocks from the Pathfinder landing site, located at the mouth of Ares Vallis, are believed to have been deposited in the late Hesperian as part of an ancient outflow episode sourced in the Martian southern highlands. The source region of these outflow deposits could range in age from early Noachian to early Hesperian (Ward et al., 1999; Tanaka et al., 2005). The age of soil samples from the various landing sites is uncertain; much of the soil present on Mars may have been emplaced during early bombardment of the Martian surface (Gooding et al., 1992), but physical weathering is an ongoing process on Mars, and formation of new soil materials via processes such as mass wasting, aeolian abrasion of rocks, and meteorite impact may be continuing at the present day.

In the case of Gusev Crater (MER-Spirit) and Ares Vallis (Pathfinder), if one makes the simplifying assumption that the rock samples analyzed at these sites have been exposed to the environment since their time of emplacement, then these rocks have experienced minimal chemical alteration over the course of billions of years. Likewise, if the bulk of the soil present at the Martian surface was formed early in Martian geologic history, then the soils analyzed during the MER, Pathfinder, and Viking missions have experienced minimal chemical alteration as well. Compared to the very young age of emplacement of the protoliths of terrestrial weathered rocks, it is clear that the nature and extent of chemical alteration on the two planets is vastly different. Estimates of physical erosion rates at the Pathfinder and MER landing sites indicate that the Martian surface environment has been a dry, desiccating one for billions of years of its geologic history (Golombek and Bridges, 2000; Golombek et al., 2006). Data for chemically altered rocks and soils at the Viking, Pathfinder, and MER landing sites are entirely consistent with such an environment, and insofar as landed mission sites can be taken as globally representative, these data suggest that low-pH, low water to rock ratio conditions have been the defining characteristic of the Martian aqueous environment over at least the past ~3.5 Ga of its history.

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