

## A GLOBAL VIEW OF MARTIAN WEATHERING BASED ON LANDER, GRS, AND MGS-TES DATA.

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**Introduction:** On the basis of geochemical analyses of Martian rocks and soils, it is becoming increasingly clear that surficial 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, 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 ( $\pm$  Fe, Ca)-sulfates and Fe-oxides. Here, we present an integrated view from landed (Viking, Pathfinder, MER) and orbital (Odyssey GRS and MGS-TES) missions, which indicates 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.

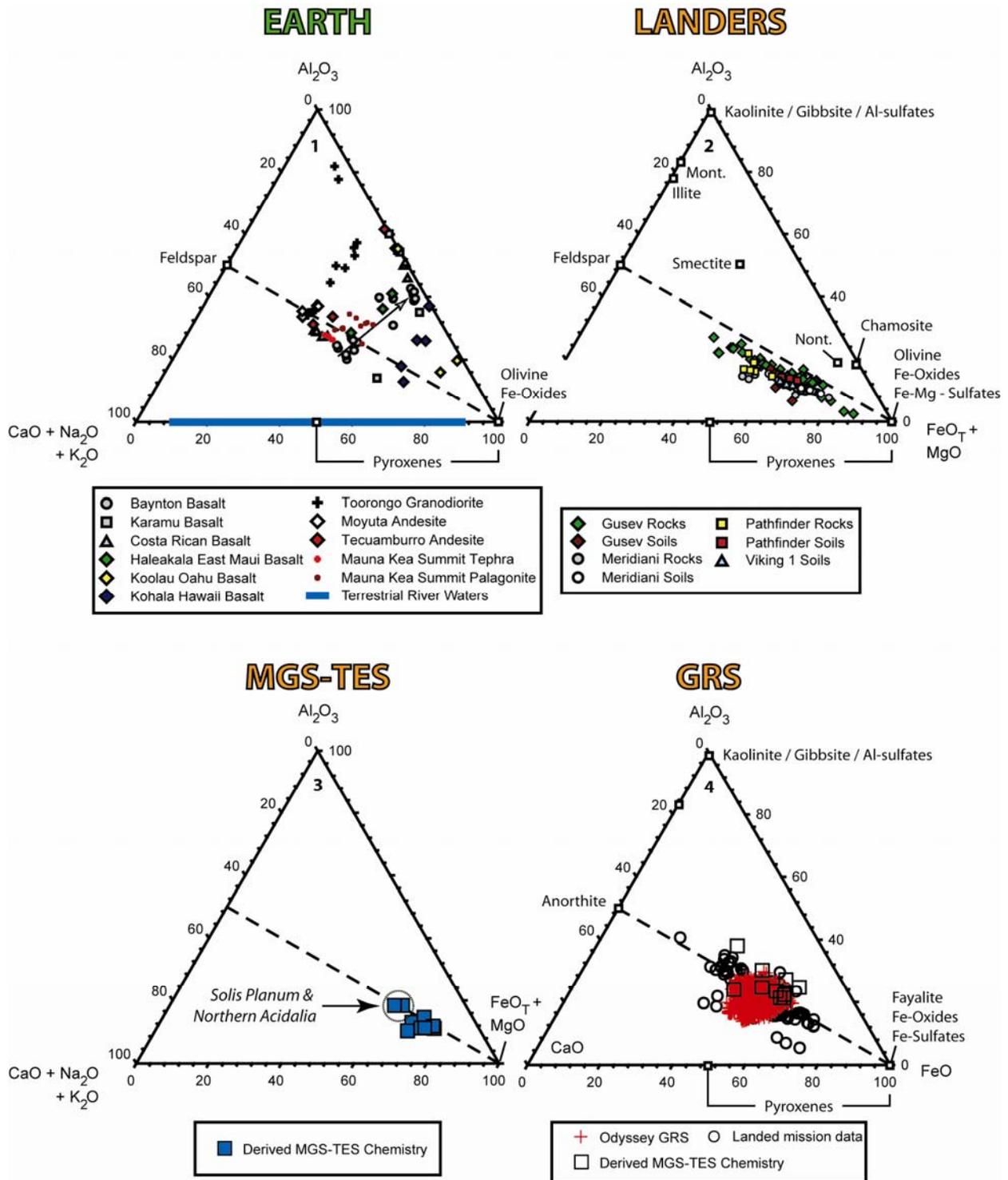
**Data Sources:** Data for the major element chemistry of igneous rocks weathered in the terrestrial environment were taken from the studies of Moon and Jayawardane [1], Morris et al., [2], Nesbitt and Wilson [3], Nesbitt and Markovics [4], Patino et al., [5], and Sak et al., [6]. These data include granodioritic, andesitic, and basaltic compositions of varying crystallinity. Data for the major element chemistry of terrestrial river waters was taken from Meybeck [7], and represent rivers draining various plutonic and volcanic terranes ranging in composition from granitic to peridotitic.

Data for the major element chemistry of Martian samples from the Viking, Pathfinder and MER landing sites are taken from Clark et al., [8], Foley et al., [9], Gellert et al., [10], Rieder et al. [11], and Gellert and Rieder [12]. Odyssey GRS data for the elements aluminum, calcium and iron are derived from gamma rays produced by neutron scattering and capture in the Martian regolith, as described by [13]. The data are smoothed with a 15-degree box car filter and binned to 5x5 degree grid points. For reasons explained in [13]

the data are confined to equatorial Mars between approximately 52.5 N and 52.5 S latitude. Typical uncertainties for each grid point are 20% (relative) for Ca and Al, and 10% for Fe. MGS-TES chemical compositions are calculated from deconvolved modal mineralogies (vol. %) by combining the compositions of the spectral endmembers (wt. % oxides) in proportion to their relative modeled abundances [14]. Wyatt et al. [15] quantified the uncertainties in derived chemical compositions and demonstrated their use in correctly classifying volcanic rocks. The one-sigma standard deviations of the absolute differences between measured and modeled major oxide abundances range from 0.4 to 2.6 wt. % [15,16]. Samples from these Martian datasets are known to include relatively fresh igneous rock surfaces, rock alteration rinds, dust/soil covered rock surfaces, basaltic soils, and at Meridiani Planum, evaporite-cemented sandstones.

**Major Element Chemistry of Weathered Rocks on Earth:** On Fig. 1 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. Unweathered igneous rocks plot in the lower left hand portion of the diagram (below the dashed line). Variation in primary igneous composition is expressed as a linear trend sub-parallel to the feldspar - (FeO<sub>T</sub> + MgO) join (dashed line on Fig. 1), 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. 1 as a linear trend from unweathered igneous rock (below the dashed line) towards the Al<sub>2</sub>O<sub>3</sub> - (FeO<sub>T</sub> + MgO) axis. This alteration trend is roughly perpendicular to the trend of primary igneous variation. The chemical alteration trajectory demonstrated on Fig. 1 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 [17]. 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 [17]. Because water-rock interactions at moderate pH result in the removal of Mg, Ca, Na, and K from igneous rocks, natural waters become en-



**Figures 1-4:** Al<sub>2</sub>O<sub>3</sub>, (CaO + Na<sub>2</sub>O + K<sub>2</sub>O), (FeO<sub>T</sub> + MgO) diagrams, data plotted in mole %. **Fig. 1** Weathered terrestrial igneous rocks. **Fig. 2** Martian rocks and soils from Viking 1, Pathfinder, and MER. **Fig. 3** Derived MGS-TES chemical abundances. **Fig. 4** Al<sub>2</sub>O<sub>3</sub>, CaO, FeO<sub>T</sub> diagram for Odyssey GRS data. Sodium and magnesium are not plotted since these elements are not analyzed by the instrument. Data from Figs. 2 and 3 are plotted on Fig. 4 to demonstrate that the systematics of Fig. 4 are similar to Figs. 1-3. Nont. = nontronite, Mont. = montmorillonite. Grey arrow indicates alteration trajectory for terrestrial weathering processes.

riched in these elements, and river waters accordingly plot along the  $(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}) - (\text{FeO}_T + \text{MgO})$  axis on Fig. 1. 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, gibbsite) and ferric iron oxides (e.g., goethite, hematite). For reference, a number of these important secondary phases are shown on Fig. 2. As shown on Fig. 1, 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 Koolau Oahu basalt, and all intermediate compositions.

**Major Element Chemistry of Weathered Rocks on Mars:** In contrast to the data presented for weathered terrestrial rocks, Martian rocks and soils do not give any indication that chemical alteration processes on the Red Planet are readily comparable to those occurring in the terrestrial environment (Figs. 2, 3, and 4). The variation amongst Martian samples from Viking, Pathfinder, MER, Odyssey-GRS, and MGS-TES appears to mimic primary igneous variation, expressing itself as scatter sub-parallel to the feldspar –  $(\text{FeO}_T + \text{MgO})$  join. And yet, the rock and soil analyses plotted on Figs. 2-4 *do not* solely represent igneous rocks. These marked differences in the elemental compositions of rocks and soils on Earth and Mars raises the question: what is different about chemical weathering processes on these two planets?

One significant difference between terrestrial and Martian alteration processes may be the in the pH at which water-rock interactions take place. Unambiguous evidence for low-pH conditions on Mars has been provided by the MER rovers at Gusev Crater and Meridiani Planum, where both Mössbauer spectrometers have detected abundant ferric-sulfate minerals, including jarosite, in both rocks and soils [18,19]. This important class of minerals forms exclusively at low-pH. Of global significance, the abundance of the nanophase Fe-oxide component in fine, wind-blown dust at both landing sites correlates positively with  $\text{SO}_3$  content, demonstrating that ferric sulfate is also present in this globally distributed material [20].

It has long been suspected that low-pH conditions have been important in alteration processes in the near-surface environment on Mars [21-23]. Hurowitz et al [24] demonstrated that much of the chemical variation displayed by rocks and soils at landed mission sites (Fig. 2) was consistent with low-pH dissolution of olivine and the resulting precipitation of Fe-Mg sulfates and Fe-oxides. Recent laboratory alteration experiments conducted at low-pH have confirmed that

this process may exert a significant control on the chemical composition of Martian soils and rocks [25-27].

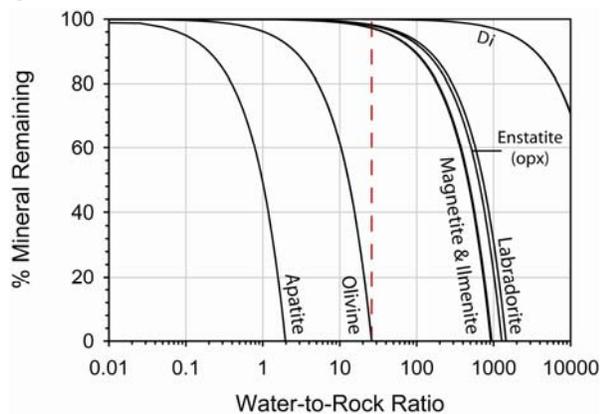
The global data from TES and GRS show that these observations apply to the entire crust, not only to the landing sites. Odyssey GRS compositions plot close to the  $\text{FeO}_T$ -plagioclase line on Fig. 4, consistent with the previously discussed relationships. TES derived chemical compositions provide no evidence for significant phyllosilicate minerals (Fig 3), however there is evidence at N. Acidalia and Solis Planum for amorphous Si-Al-rich coatings developed under conditions of incipient alteration [28,29]. Taken together, these observations from both the laboratory and the Martian surface indicate that acidic conditions have played a significant role in the modification of Mars' basaltic crust.

**Aluminum Mobility and Implications for Water-to-Rock Ratio:** Based on the relationships shown for terrestrial data (Fig. 1) it is clear that variations in Al 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 residual enrichment of Al in weathered rocks and formation of abundant clay minerals and Al-hydroxides.

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 [17]. Sulfuric acid-rich conditions would promote the formation of Al-sulfate minerals, which plot at the  $\text{Al}_2\text{O}_3$  apex of Figs. 1-4. The formation of Al-sulfate has been demonstrated experimentally during low-pH, sulfuric acid-rich alteration of olivine-poor basalts under Martian conditions [25,26,30]. The data plotted on Figs. 2-4, 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 Figs. 2-4 provide any indication that clays or Al-hydroxides are an important component of the secondary mineral budget on Mars, though it may 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 Mars Express [31,32].

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. 5, a plot of % mineral remaining against water-to-rock ratio. The diagram assumes 1kg of basalt reacting with a pH = 2

fluid in a system that is continuously re-supplied with fresh acid. The modal mineralogy of average Adirondack class basalts from McSween et al. [33] was used to partition the mass fraction of minerals in the basalt. We note that the value calculated for 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. As shown, 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 ~25. At this point, only about 1-3% of the other minerals present in the rock have been dissolved, including plagioclase, the primary source of Al. We therefore hypothesize that the lack of significant Al-bearing secondary mineral phases inferred from the relationships shown on Figs. 2-4 are the result of an alteration environment on Mars which is characterized by 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. Taylor et al., [34] demonstrated a uniform K/Th signature for GRS data; the lack of significant K-fractionation is also consistent with insignificant plagioclase dissolution.



**Fig. 5:** Plot of % mineral remaining against water-to-rock ratio. Modeled mineral dissolution curves were constructed with an equation used in laboratory experiments to calculate mineral dissolution rates in a continuously-stirred tank reactor.

**Summary:** Chemical data from landed mission sites and orbital instruments, which sample across a variety of depth scales from 10's of meters (e.g., exposed stratigraphy at Meridiani Planum) to 10's of microns (sampling depth of MGS-TES), provide a consistent picture of chemical weathering processes across the Martian surface. These weathering processes appear to be fundamentally different from those

operating in the terrestrial environment. Comparison of the geochemical data returned from landers, Odyssey GRS, and MGS-TES to laboratory data indicates that low-pH, low water-to-rock ratio alteration of basaltic materials exerts a significant control on the chemical composition of rocks and soils on Mars. The important role these processes play are entirely consistent with evidence for abundant ferric-sulfate minerals, and a lack of significant Al-mobilization and/or fractionation into secondary minerals at the Martian surface.

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