EXPERIMENTAL BASALT ALTERATION AT LOW-pH: IMPLICATIONS FOR WEATHERING RELATIONSHIPS ON MARS.

J.A. Hurowitz[1], N.J. Tosca[1], S.M. McLennan[1], and the Athena Science Team. [1]Department of Geosciences, State University of New York at Stony Brook, Stony Brook, NY 11794-2100 (joel.hurowitz@stonybrook.edu).

Introduction: The chemistry of sedimentary rocks has long been utilized for the reconstruction of climatic, geographic and tectonic conditions in the Earth's past [1]. Naturally, the chemical and mineralogical changes that accompany weathering of the Earth's granodioritic upper crust have been studied in great detail to better understand processes controlling the composition of sedimentary rocks [2]. Weathering of basaltic rocks has been studied as well, and there is a reasonable understanding of the bulk chemical and mineralogical changes that accompany alteration of such rocks under terrestrial conditions [3]. In contrast, Martian soils and altered rocks, which undoubtedly reflect the end product of some combination of physical and/or chemical alteration, do not appear to have evolved in a manner consistent with alteration of basalts as we know it on Earth [4]. Here we present new insights into weathering processes on Mars utilizing the results of alteration experiments performed at low-pH on synthetic basalts of Martian composition [5, 6].

The Effect of pH on Weathering Processes: Shown on **Fig.1** is a ternary diagram commonly used to predict the major element and mineralogical composition of weathering profiles generated on primary igneous rocks [7]. Plotted are data for the Baynton basalt [3] and Toorongo granodiorite [2] weathering profiles, both developed in temperate climates in Australia. The primary compositional variability of igneous rocks follows a trend subparallel to a tie line drawn between feldspar and the $FeO_T + MgO$ apex.

The weathering trends (dashed arrows), indicate that the main consequence of weathering on Earth is to leach primary igneous minerals of the soluble elements Ca, Na, Mg, and K, while enriching the weathering profile in the insoluble elements Al and Fe (III). These weathering trends are developed primarily as a result of one major factor: the pH of waters altering primary igneous rocks at the Earth's surface.

The pH (=5-8) of most terrestrial waters fall at or near the solubility minima of Al and Fe (III) with respect to common low-temperature secondary mineral phases [8]. In addition, at pH values $\geq \sim 4$ the rate of iron oxidation increases 100-fold for every unit increase in pH, whereas for pH $\leq \sim 4$, the rate of iron oxidation is constant [8]. As a result, any Fe (II) released to solution oxidizes rapidly (compared to low-pH environments) to insoluble Fe (III) in most natural waters on Earth. The end result of these pH driven effects is that as alteration occurs, Al and Fe released to solution from primary mineral dissolution rapidly precipitates in the form of secondary minerals, enriching weathering profiles in Al and Fe (III).

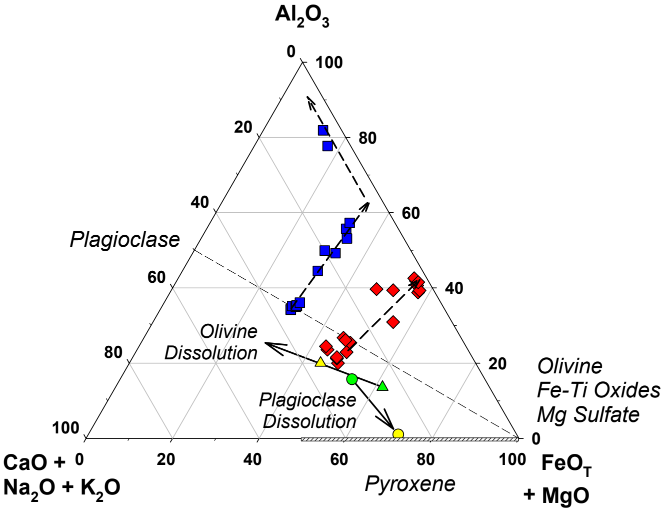

Fig. 1: Blue squares are for terrestrial granodioritic weathering profiles, red diamonds for basaltic profiles. Green triangle: unaltered synthetic olivine bearing basalt, yellow triangle: altered at low-pH. Green circle: unaltered olivine-free synthetic Los Angeles shergottite, yellow circle: altered at low pH.

Low-pH Alteration: On Mars, it is generally accepted that the high concentrations of S and Cl in the Martian soils are consistent with the presence of a salt component formed in a low-pH environment [9]. This has led to the general conclusion that aqueous fluids are dominantly acidic in the Martian surface and shallow subsurface. In experimental studies by Tosca et al. [6] and Hurowitz et al. [5], synthetic basalts of Martian composition were experimentally altered under low-pH (=1-4) conditions in order to ascertain the nature of secondary minerals produced by alteration of Martian basalts in acidic environments.

From these studies, the composition of basaltic residues remaining from alteration at low-pH can be calculated from published values for starting basalt compositions and fluid compositions produced during alteration. These calculated residual compositions can be used to predict the chemical fractionation that accompanies basalt alteration at low-pH in the natural environment on Mars, in much the same way as for terrestrial weathering profiles. The results of these calculations are shown on **Fig.1**, which compares the chemical fractionation trends generated in terrestrial weathering profiles, to those generated at low-pH.

The trend generated by synthetic olivine-bearing Martian basalt alteration at low-pH is nearly perpendicular to that observed for terrestrial weathering profiles (**Fig.1**). For the pH (=1.0) and W/R (=10) which the experimental trend was generated, release of cations to solution is controlled by the fastest dissolving mineral phase present in the basalt: olivine. Similarly, for dissolution of a synthetic olivine-free Los Angeles basaltic shergottite at pH=1.0 and W/R=1000, release of cations to solution is controlled by dissolution of labradorite, again resulting in an alteration trend nearly perpendicular to terrestrial weathering trends. These chemical changes result from the fact that at low pH, Fe oxidation is kinetically inhibited and Al^{3+} is far more soluble than at near neutral pH. As a result, the basalts are stripped of these elements (which are normally considered immobile relative to Ca, Na, K, and Mg), and they do not readily precipitate as insoluble ferric or aluminous phases, in contrast to terrestrial weathering.

Comparison to Martian Rocks and Soils: Using the experimental alteration trends as a guide, differences between brushed and RAT-ed surface analyses of the Gusev plains basalt “Adirondack” can be interpreted in terms of low-pH alteration processes, as shown on **Fig.2**. The difference between the RAT-ed (rock interior) and brushed (soil-free rock surface) compositions are consistent with a low degree of olivine dissolution of Adirondack to form an altered surface represented by the brushed rock analysis. The rock Humphrey (not plotted) shows the same behavior.

Similarly, the Pathfinder rock analyses appear to have evolved along the same olivine removal trend, indicating a higher degree of alteration than either Adirondack or Humphrey (assuming the Pathfinder rocks started out with a Gusev basalt-like chemistry). These relationships have important implications for the interpretation of the chemistry of the Pathfinder rocks, which have previously been interpreted as a mixture between unaltered igneous rock and soil [11].

Soil analyses from the Gusev, Pathfinder and Viking-1 landing sites also appear to align along the experimental olivine dissolution trend. Note, however, that the addition of Mg-sulfates and/or Fe-oxides to soils will have the opposite effect to olivine dissolution on **Fig.2**, pulling analyses towards the lower right apex of the diagram. Both of these minerals are thought to be important components of the Martian soils [12], so it is not unexpected that individual soils should be variably mixed with either or both of these phases.

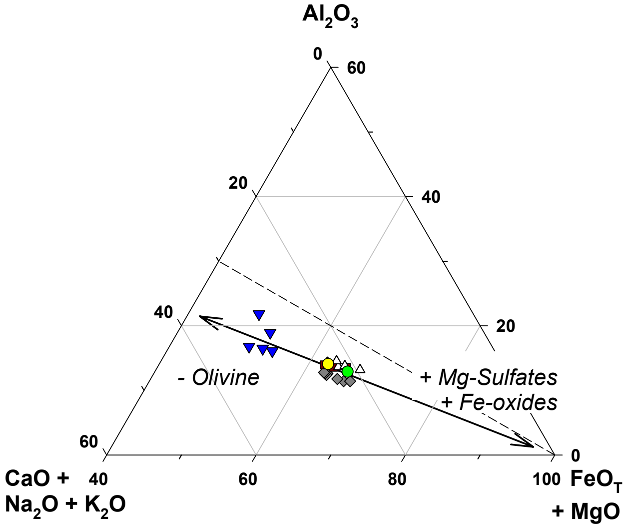

Fig. 2: Green circle: RAT-ed Adirondack, yellow circle: brushed [10]. Blue triangles: Pathfinder rocks [11], red squares: Gusev soils [10], white triangles: Pathfinder soils [11], grey diamonds: Viking soils [9].

Conclusions: The effects of alteration at low-pH produce fundamentally different major element relationships from those expected for alteration under typical conditions on Earth. This is a result of the fact that at low-pH, Al and ferric iron are highly soluble, and the oxidation rate of ferrous iron to less soluble ferric iron is far lower than in the pH range of natural waters on Earth. In effect, the elements commonly taken to be immobile in terrestrial weathering profiles (Al, Fe (III)) are mobile in the low-pH environment.

In general, chemical data from Martian rocks and soils appear to be consistent with some combination of three major processes: (1) dissolution of olivine at low-pH and W/R (2) addition of Mg-sulfate, and (3) addition of secondary iron oxides. Martian rocks and soils do not mimic the weathering trends produced by basalt alteration on Earth, indicating they have not been altered by interaction with large volumes of moderate pH rainfall or groundwater.

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