UNDERSTANDING MARTIAN ALTERATION PROCESSES BY COMPARING IN-SITU CHEMICAL MEASUREMENTS FROM MULTIPLE LANDING SITES.

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Introduction: Characterizing the history of aqueous activity at the martian surface has been an objective of the Mars Exploration Rovers (MER) and the Mars Science Laboratory (MSL). Although the geologic context of the three landing sites are different, comparisons across the datasets can provide greater insight than using data from one mission alone. The Alpha Particle X-ray Spectrometer (APXS) is common to all three rovers (Spirit at Gusev crater, Opportunity at Meridiani Planum, and Curiosity at Gale crater) and provides a consistent basis for these comparisons.

Soil and Dust: Fine grained basaltic soils and dust are remarkably uniform in chemical composition across multiple landing sites. These similarities in the concentrations of major, minor, and a few trace elements (Fig. 1) are indicative of planet-wide consistency in the composition of source materials for the soils. S and Cl vary by a factor of two in the soil and dust, but there is no clear association with any bulk cation (e.g., no correlation between S and total Ca, Mg, or Fe in soils). These volatile elements, however, are clearly associated with the nanophase-ferric iron component in the soil established by Mössbauer spectroscopy [1,2]. S and Cl likely originated as acidic species from volcanic outgassing and subsequently coalesced on dust and sand grain surfaces, possibly with an affinity towards Fe^{3+} sites. Importantly, given the mobility of S and Cl in aqueous exposures, soil samples maintaining the typical molar S/Cl ratio of ~3.7:1 indicate minimal interactions with liquid water after the addition of S and Cl. In contrast to this well-established baseline, soil samples have been discovered at all three landing sites with atypical S/Cl ratios (e.g., subsurface soils), indicative of a more complex aqueous history.
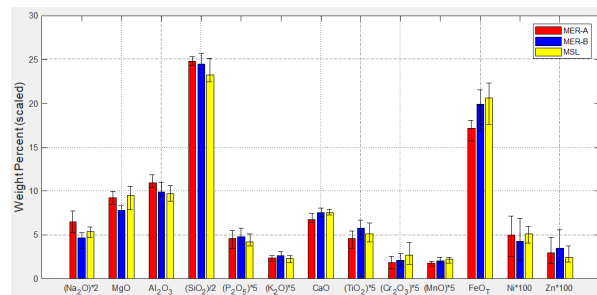

Fig. 1: Average chemical composition for basaltic soils shown on an S-Cl-Br-free basis (some values scaled; $N_{samples}>30$ for each landing site).

Unaltered Samples: In conjunction with the appropriate geologic context, Fe/Mn ratios calculated from APXS data can help identify unaltered rocks and soils. Fe^{2+} and Mn^{2+} have nearly the same ionic radii and distribute similarly in primary igneous rocks, maintaining a consistent Fe/Mn ratio for unaltered samples. Upon exposure to alteration environments, higher oxidation states of Fe and Mn are commonly formed. Differing mobility of these species results in elemental fractionation. The average molar Fe/Mn ratio for unaltered materials is 48±3 (Fig. 2), representing units such as the Gusev basalts, the Stimson sandstone (Gale), and basaltic soils at all landing sites. Note that the APXS measures total Fe (Fe^{2+} and Fe^{3+}), so the unaltered Fe/Mn ratio will have some variability with the oxygen fugacity of the igneous system. Variability in the Fe/Mn ratio for other samples (Fig. 2) is indicative of aqueous alteration and mobility of Fe and/or Mn away from the unaltered baseline (e.g. Meridiani spherules).
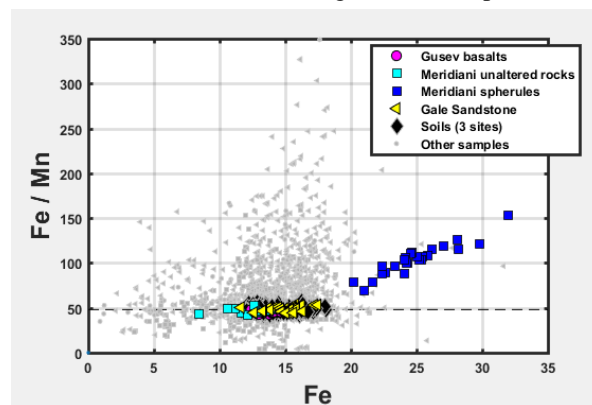

Fig. 2. Molar Fe/Mn ratio versus Fe. Samples along the dashed line maintain an unaltered Fe/Mn ratio.

Surface Coatings: Rocks at the surface of Mars, especially those which appear to have been exhumed, exhibit surface coatings rich in S and Cl, and occasionally Zn and Ni (Fig. 3). These enhancements are not simply due to insufficient removal of dust accumulations as the S/Cl ratios or other chemical characteristics are inconsistent with a layer of dust. The formation of these rock coatings may involve water thin-films mobilizing S and Cl from dust and soil at near-subsurface cold-traps, such as the surfaces of high thermal-inertia rocks, during diurnal/seasonal cycling of water vapor. These coatings are observed at all three landing sites and likely represent a planet-wide alteration process.
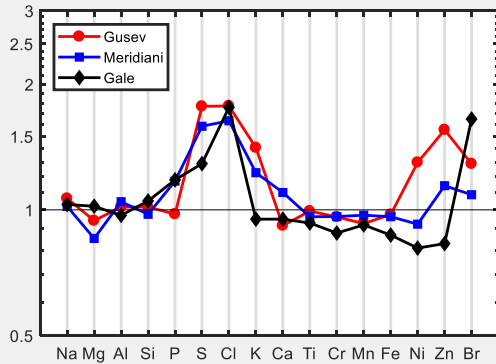
Fig. 3: Average ratios of brushed surfaces to rock interiors. Meridiani data excludes Burns formation (high SO_3), and Gale data excludes samples with >5 wt% Ca-sulfate measured by CheMin X-ray diffraction.

Sulfates: Sulfur is ubiquitous on the surface of Mars. Only ~25 of the >1500 MER and MSL APXS analyses have less than 2 wt% SO_3. Elemental correlations with sulfur indicate the presence of Ca- (Fig. 4) and Mg-sulfates. Identifications of Fe-sulfates and hydroxysulfates have also been made in conjunction with other rover instruments [2,3]. Cross-cutting Ca-sulfate veins at Meridiani and Gale indicate late-stage fluid infiltration of lithified sediments. Ca-sulfates at Gusev may be associated with other hydrothermal deposits in the environs of Home Plate.
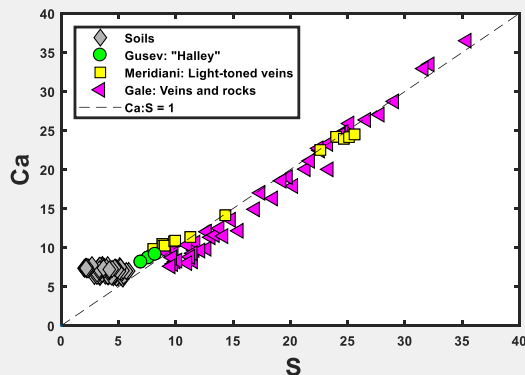

Fig. 4. Molar Ca versus S showing that Ca-sulfates are found at Gusev, Meridiani, and Gale. Dashed line (Ca:S = 1:1) represents pure $CaSO_4 \cdot nH_2O$.

High Silica Deposits: The average SiO_2 content of primary rocks on the Gusev plains and of basaltic soils is approximately 46 wt%; however, numerous samples analyzed by the APXS at each of the landing sites exhibit >55 wt% SiO_2. Pathways for achieving elevated SiO_2 concentrations in martian samples include detrital accumulations of differentiated silicic igneous rocks [4], acidic leaching of other rock-forming elements resulting in Si-rich residue [5], and precipitation of silica from the influx of Si-rich fluids [6].

Comparisons of the high-silica samples at the three rover landing sites indicate two distinct trends (Fig. 5). Many of the sample groups maintain a fairly constant Si/Ti ratio despite large increases in Si, which is a characteristic of acidic leaching. A subset of the samples from the Home Plate region of Gusev crater, on the other hand, follow a dilution trend consistent with the addition of silica to a basaltic precursor.
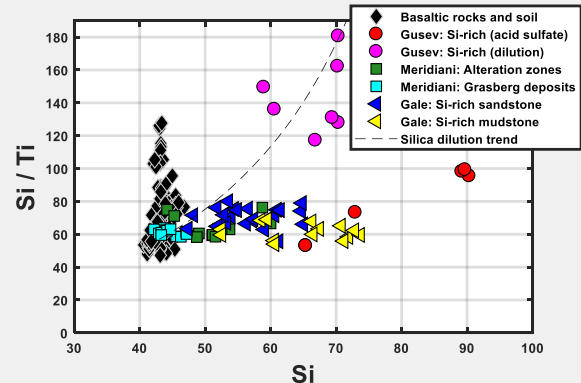

Fig. 5: Molar Si/Ti versus Si for selected samples. The dashed line represent the expected trend for the addition of silica (dilution of Ti) while flat Si/Ti ratios are consistent with acidic leaching.

Elemental Mobility: In addition to the chemical signatures of alteration described above, there is clear evidence for aqueous mobility of numerous other elements (Mn, K, Ge, Zn, Ni, P, Br) at two or more of the rover landing sites. While the same geologic conditions may not have been active for each element, comparing the circumstances of elemental enrichments/depletions across samples and missions fuel hypotheses for the nature of the aqueous episodes.

Using APXS data in conjunction with mineralogical instruments (Mössbauer for MER and CheMin for MSL), it has been discovered that certain samples with nearly identical chemistry have substantially different mineralogy. Isochemical alteration processes, likely at low water-to-rock ratios, have also been active at all three rover landing sites.

Summary: The ability to compare and contrast three cross-calibrated elemental chemistry datasets from different locations on Mars provides substantially more insight than using the data from one mission alone. Various degrees of aqueous alteration ranging from "minimal" to "extensive" have been established using rover geochemical data.

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