THE ENIGMATIC GLOBAL MARTIAN SOIL: COMPOSITIONAL EVIDENCE FROM MER, PHOENIX, VIKING, MPF, MGS AND ODYSSEY. B. C. Clark\(^1\), R. Gellert\(^2\), R. V. Morris\(^3\), D. W. Ming\(^4\), A. Yen\(^4\), R. E. Arvidson\(^2\), T. Economou\(^4\) and the Athena Science Team. \(^1\)Space Science Institute, Boulder CO, USA, \(^2\)University of Guelph, Guelph, Canada, \(^3\)NASA Johnson Space Center, Houston, TX, \(^4\)Jet Propulsion Laboratory, Pasadena, CA,

Introduction: The existence of a global soil unit on Mars has been inferred by remarkably similar elemental profiles at the initial five landing sites \([1-5]\), as well as at multiple sites of extended exploration by the MER rovers Spirit and Opportunity \([4, 5]\). Viking x-ray fluorescence analysis recorded a compositional shortfall, possibly indicative of a significant component of light elements. Orbital missions, especially Odyssey, Mars Express (MEx) and Mars Reconnaissance Orbiter (MRO), as well as the recent Phoenix lander mission have provided additional data and constraints that indicate a complex compositional makeup and history of martian soil.

Composition: The global-scale soil manifests itself by its spectroscopic uniformity and element compositional consistency, with characteristic concentration ratios such as Fe, Mg, Al, K, and Ca relative to Si. In spite of optical masking by this global soil, Mars itself is now revealed by MER, MEx and MRO missions as a geochemical hot spot in the solar system, its diversity overshadowed only by planet Earth.

In situ measurements of soils are often overprinted by detritus from surrounding rocks or sediments, now recognizable as K-enrichment from rocks at the Pathfinder site \([3]\); as P-enrichment from Wishstone - Wachtower class rocks at Husband Hill \([4]\); as Fe-enrichments from hematitic spherules at Meridiani \([5]\); and as contamination from silica and ferric sulfate whith soils in the Columbia Hills \([4]\).

Mössbauer measurements \([6]\) by the MER rovers revealed an unexpectedly high level (up to 75%) of soil Fe is in igneous mineral components, split equally between olivine and pyroxene, plus up to one-tenth magnetite and >15% as nanophase Fe\(^{3+}\)oxides.

Surficial Coating Model: Because of the lack of correlation of cations with the high S and Cl content of martian soils \([1, 7]\), it has been surmised that acidic volcanic gases containing these elements have coated airborne and exposed surface grains, perhaps as an amorphous layer which has not been fully converted to salts due to the dry cold environment. Such a coating could be as thin as 0.1 micron on a 4-micron diameter grain, and account for the S and Cl concentrations observed. More likely, these components would penetrate by surface migration into cracks or diffusion into the bulk interior, but perhaps not uniformly throughout the particles affected. Interestingly, the main cor- relate with higher S and Cl in soils has been nanophase ferric oxide measured by with Mössbauer analyses \([6]\), which also could be produced by surficial processes, via UV-stimulated photochemical oxidation of divalent Fe in mineral grains.

Viking Light Element Shortfall: The Viking x-ray fluorescence measurements had the capability to assess absolute concentrations of detected elements by use of a backscatter peak from its Cd-109 source \([2]\), whereas x-ray measurements on other missions are scaled directly to a sum of 100.0 wt% for the oxide equivalents of the elements detected by their fluorescence emissions All Viking analyses showed a shortfall in detected elements, with a sum of 89 wt% for “Average Deep Soil”, assuming all Fe as Fe\(_2\)O\(_3\) \([2]\). Various possibilities were ascribed to this shortfall, including a matrix effect related to grain size, but more likely due to a number of light elements whose emissions could not be detected. (APXS data from MER are now being examined for similar evidence by assessing backscatter, \([8]\)). Undetectable elements included the low atomic number elements (CHON, plus Li, B, F), and certain obscured elements such as the emissions from Na, P, Mn and Cr. These are variously ascribed to possible constituents such as H\(_2\)O, -OH, carbonates, nitrates, phosphates, and superoxides of Na and K \([2]\). Alpha backscatter measurements on MPF failed to detect C, N or inferable H\(_2\)O in soils above its detection limits \([3]\).

Also hypothesized have been chlorates, bromates, and oxidation states of S higher than sulfate \([9]\). Oxidants in soils could have obscured evidence for organics by reacting with them during the pyrolysis experiments of the GCMS instruments on Viking and the TEGA instrument on Phoenix. Meteoritic components, possibly present at a level of a few per cent as reflected by the observed Ni content \([1]\), could provide a small amount of reduced Fe and S, but these have likely been oxidized by exposure to photochemical oxidants in the atmosphere (although Fe meteorites discovered by MER Opportunity appear to have suffered minimal alteration).

Important discoveries since Viking include high levels of Na and P in MER soils; significant H\(_2\)O-equivalent concentrations (inferred from measured H) of ~ 3 wt % in Viking terrains by Odyssey gamma ray and neutron remote observations \([10]\); confirmation of
carbonate by IR spectral observations of dust [11], thermal evolved gas analysis in Phoenix soils [12, 13] and measurement of alkaline pH consistent with Ca carbonates; discovery of perchlorate by the Phoenix MECA wet chemistry lab [14], bringing 3.5 oxygen atoms per chlorine atom into the tally; and detection of Fe^{3+} by MER rovers [6] as nanophasic ferric oxide and magnetite, with Fe^{3+}/Fe_{tot} ratios in the range of 0.2 to 0.4 for soils. Fine-grained materials will adsorb and possibly chemisorb H_2O from the atmosphere. Water of hydration of salts has also been implicated as an important repository of H_2O, including hydrates of MgSO_4, ferric sulphates and now perchlorates [14]. Clay minerals have not been detected at significant levels in soils but are present in certain regional deposits discovered by MEx and MRO.

These additions help to explain the Viking light-element deficit and add to the credibility of a Mars that is intrinsically rich in volatile elements, having important implications for climate, astrobiology and geochemistry.

Mössbauer measurements attest to the presence of Fe-bearing igneous minerals in soils [6]. Microscopic imaging by MER and Phoenix clearly show that soils can contain significant components of discrete lithic fragments or mineralogical grains, some fraction of which must be transported only locally or regionally by saltation, rather than globally distributed by aeolian activity. Widespread dust devil activity on Mars can augment the mobilization of larger particulates. On the other hand, duricrusts are also common on Mars and the long term stability of some dune fields attest to inactivity, possibly due to weak but sufficient cementation between grains. The magnetic fraction of airborne dust has been shown to contain titanomagnetite, as well as olivine grains and ferric oxides [15].

Conclusions: The Viking shortfall in accountable components can be explained by various constituents now detected in martian soils by other missions, especially including carbonates, hydration, and perchlorates. The lack of deep chemical alteration of the global soil unit indicates that the genesis of this intriguing material post-dates the warmer wetter climates of the Noachian era and perhaps later periods. Apparently, the intervening time period has consistently experienced low water activity and perhaps been dominated by photochemically-mediated surficial alteration processes.

Nonetheless, because of the intensity and global nature of quasi-annual dust storms over millions of years, this unit presumably comprises a widespread sampling of numerous igneous and sedimentary units exposed at the surface of the planet. Identification of all the components in martian soils remains challenging and a high priority for future exploration, and may someday provide the broadest insights into the varieties of source materials and past environments on Mars.

References: