

ZINC AS AN INDICATOR OF ALTERATION AT THE MARTIAN SURFACE. A. S. Yen¹, B. C. Clark², R. Gellert³, R. V. Morris⁴, J. A. Hurowitz¹, and the Athena Science Team. ¹Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109 (Albert.Yen@jpl.nasa.gov), ²Lockheed Martin Corporation, Littleton, CO 80127, ³University of Guelph, Guelph, ON, Canada, ⁴NASA Johnson Space Center, Houston, TX 77058.

Introduction: Data from the Alpha Particle X-ray Spectrometers (APXS) [1] onboard the Mars Exploration Rovers (MER) provide a revolutionary view of the diversity of chemical compositions at the martian surface. Major, minor, and trace element signatures obtained from approximately 300 distinct measurements on Mars establish relationships (or lack thereof) between rocks, between soils, and between rocks and soils [e.g., 2-4]. Zinc is one of the elements that has been unambiguously detected (Figure 1), and measured concentrations approach 2300 ppm. The systematics of Zn observed in martian samples show that it is a likely product of volcanic emissions and is useful as a tracer for certain weathering processes at the surface of Mars.

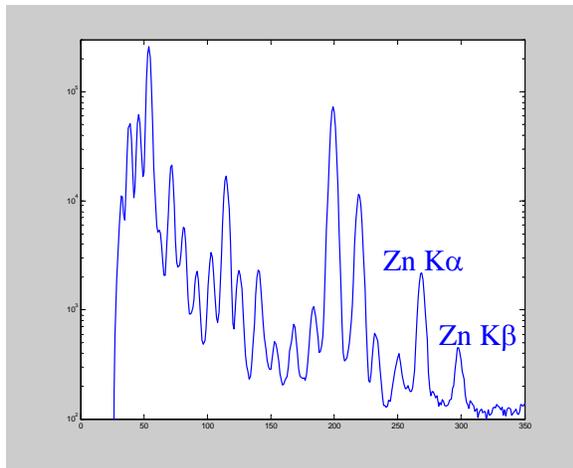


Figure 1: Example of raw APXS data with clear indications of Zn K-alpha and K-beta x-ray peaks.

Volcanic Emissions: The presence of sulfur and chlorine in the martian regolith has long been attributed to condensation of volatiles emitted from volcanic events [5-7]. The APXS data from MER clearly support these earlier conclusions, as the observed ratio of S to Cl is nearly constant for the majority of soil samples analyzed at Gusev Crater and Meridiani Planum, which are separated by approximately 180 degrees of longitude (Figure 2). This result indicates that a planet-scale process is likely responsible for the distribution of S and Cl in these soils.

Data from the APXS indicate that zinc is also associated with the S (Figure 3) and Cl in martian soils. The fourth component of this family is the nanophase

iron oxyhydroxides (np-Ox) detected by the Mössbauer spectrometer [e.g., 8] (Figure 4). Thus, S, Cl, Zn, and np-Ox are all well-correlated in martian soils.

No distinct sulfate, chloride, or zinc mineral phase, however, is present in these soils. Figure 5 illustrates ratios of the high S soil endmembers against those with low S. As expected, Cl and Zn are elevated in association with S, but there is no clear cation associated with the ~several wt% variations in S and Cl. Zn does not suffice as the cation, as the concentrations are too low. The likely scenario consistent with these results involves condensation of S, Cl, and Zn on the surfaces of soil grains where these elements originated as SO₂, H₂SO₄, HCl, and ZnS from volcanic emissions. The acidic volatiles likely produced localized sulfates and chlorides on the grain surfaces and acted to oxidize a subset of the iron. Note that typical martian soils remain dominated by ferrous iron with a ferric to total iron ratio of approximately 0.35, so the extent of alteration is likely limited to the surfaces of the soil grains.

The nearly constant relationship between S, Cl, and Zn indicate that the majority of the soil samples analyzed by MER have not experienced significant weathering after the volcanic event(s) that contributed these elements. Exposures to water would have rapidly redistributed soluble sulfates and chlorides producing a different ratio of these elements, which is suggested in certain examples of subsurface soils [9].

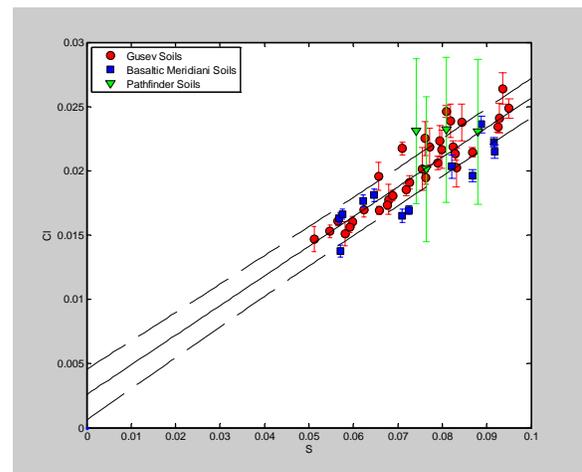


Figure 2: Linear relationship between sulfur and chlorine in Gusev, Meridiani, and Pathfinder soils is a clear indication of a global process.

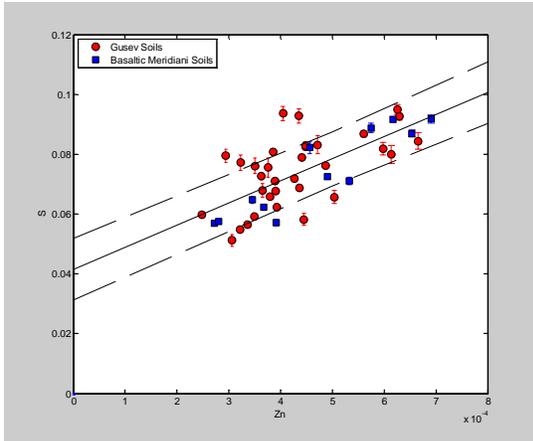


Figure 3: Correlation between sulfur and zinc in martian soils. Note that typical concentrations of Zn are approximately two orders of magnitude lower than S.

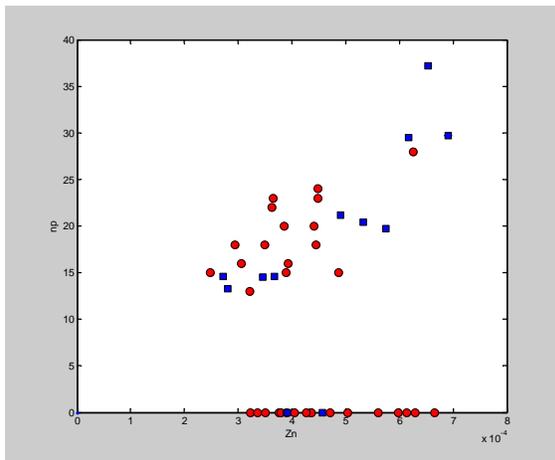


Figure 4: Correlation between nanophase ferric iron oxyhydroxides (np-Ox) and Zn in martian soils. Points along the x-axis are samples without Mössbauer data.

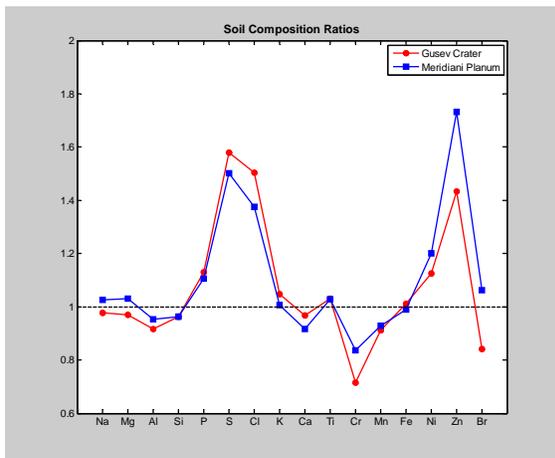


Figure 5: Ratio of high S, Cl, Zn soils to samples with low concentrations of these components. No other element is clearly associated with these components.

Isochemical Weathering: A family of rocks referred to as "Wishstone" and "Watchtower" classes (Figure 6) at Gusev Crater are distinctly characterized by elevated P and Ti with Cr at or near the detection limit [4, 10]. These rocks are approximately isochemical but, as established by the Mössbauer spectrometer, exhibit ferric to total iron ratios (Fe^{3+}/Fe_T) ranging from 0.25 to 0.94 [8]. In these samples, Zn is correlated with Fe^{3+}/Fe_T (Figure 7), as well as with the dominant Fe^{3+} components individually: Np-Ox (nanophase ferric oxyhydroxides) and hematite. These observations indicate that Zn is a tracer for weathering.

One possible scenario for the alteration of these rocks involves interactions with volcanic gases. Emissions from nearby vents may have interacted with the more weathered samples, oxidizing the iron and depositing Zn. Alteration by water (rather than a purely thermal event), possibly originating in a vapor phase, is indicated by the presence of goethite ($\alpha-FeOOH$) in the more extensively altered samples [8]. This alteration process necessarily occurred at low water-to-rock ratios given the nearly isochemical nature of the samples. That is, if larger volumes of water were available, the more soluble elements would have been mobilized in the weathered samples and the elemental signatures would not remain nearly constant.

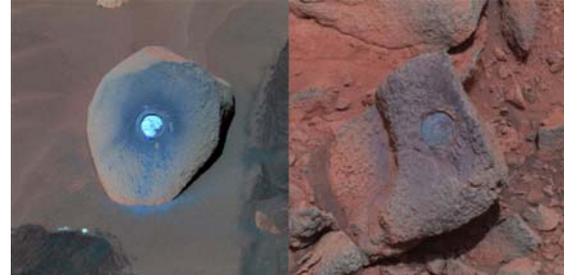


Figure 6: Wishstone (left) and Watchtower (right) samples are similar in elemental chemistry, but Watchtower is extensively weathered relative to Wishstone.

Zinc and Hematite: The highest concentration of zinc measured by the APXS on Mars (~2300 ppm) is of the sample Halley (Figure 8), which also has one of the highest percentages of hematite found in samples analyzed by the Mössbauer spectrometer (~70% of the Fe). The Fe^{3+}/Fe_T of Halley is approximately 0.9, indicating an extensively oxidized sample. Ca-sulfate is likely present in Halley (Figure 9), and Zn and Cl are also closely associated in this sample (Figure 10). Alteration of Halley, possibly through aqueous processes, is clearly suggested by this evidence. The high concentrations of Zn in this weathered sample provide additional evidence that this element is an indicator of alteration processes.

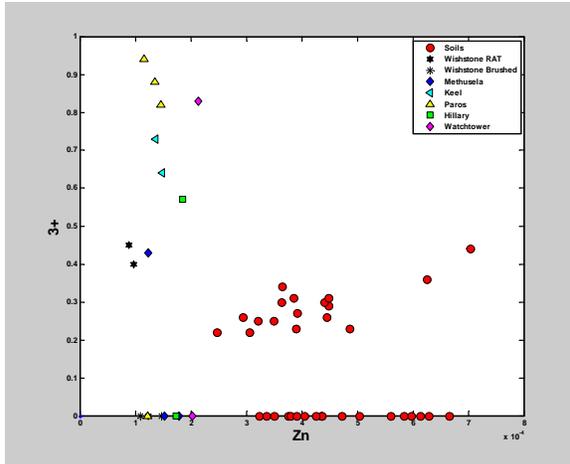


Figure 7: Ferric to total iron ratio plotted versus zinc for the Wishstone/Watchtower family of rocks and for typical Gusev soils. Points along the x-axis represent samples where Mössbauer data were not collected.

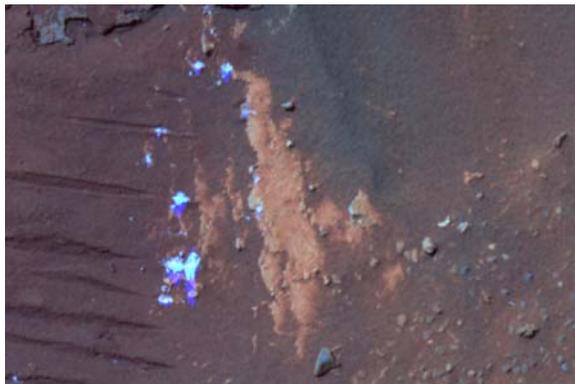


Figure 8: False color Pancam image of the sample "Halley." The bright portions of the image represent regions of the sample disturbed by the rover wheels.

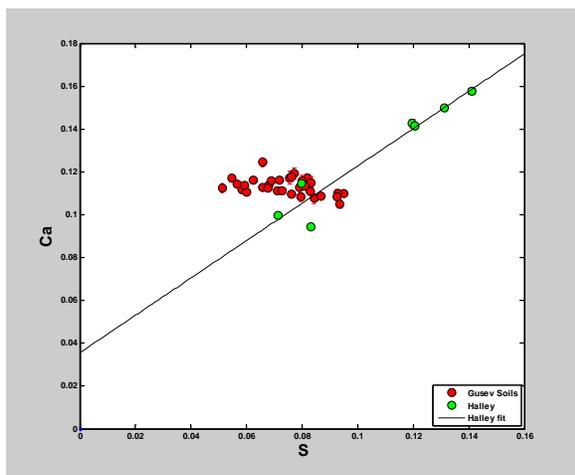


Figure 9: Ca versus S for typical Gusev soils and for Halley. The presence of Ca-sulfate ($Ca:S \sim 1$) in Halley is clearly indicated.

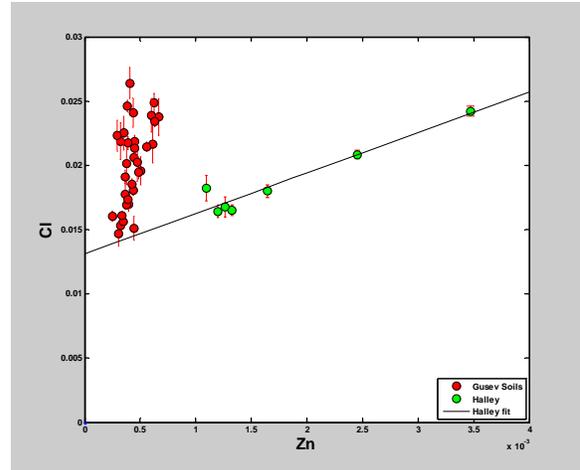


Figure 10: Zinc concentrations in Halley are substantially greater than found in typical soils and are clearly associated with Cl.

Conclusions: Zinc, sulfur, and chlorine are well correlated in the majority of martian soils with no indications of other elemental associations. These soil constituents are likely condensates of volcanic outgassing. The approximately constant relationships indicate that the extent of aqueous weathering of typical martian soils after the volcanic event(s) which contributed these elements has been minimal to non-existent.

Zinc is correlated to the ratio of ferric to total iron in a variety of samples where the ferric iron is present as a nanophase oxide/hydroxide or as hematite. This indicates that Zn may be used as a tracer for alteration of martian surface materials.

References: [1] Rieder R. et al. (2003) *JGR*, 108, 8066. [2] Gellert R. et al. (2004) *Science*, 305, 829-832. [3] Rieder R. et al. (2004) *Science*, 306, 1746-1749. [4] Gellert R. et al. (2006) *JGR*, 111, E02S05. [5] Clark B. C. and Baird A. K. (1979) *JGR*, 84, 8395-8403. [6] Banin A. et al. (1997) *JGR*, 102, 13341-13356. [7] Nelson M. J. et al. (2005) *GCA*, 69, 2701-2711. [8] Morris R. V. et al. (2006) *JGR*, 111, E02S13. [9] Haskin L. A. et al. (2005) *Nature*, 436, 66-69. [10] Clark B. C. (2007), *in preparation*.