## SILICA RETENTION AND ENRICHMENT IN OPEN-SYSTEM CHEMICAL WEATHERING ON MARS. A. S. Yen<sup>1</sup>, D. W. Ming<sup>2</sup>, R. Gellert<sup>3</sup>, B. C. Clark<sup>4</sup>, D. W. Mittlefehldt<sup>2</sup>, R. V. Morris<sup>2</sup>, L. M. Thompson<sup>5</sup>, J. Berger<sup>6</sup>, MSL and Athena Science Teams, <sup>1</sup>JPL/Caltech, <sup>2</sup>NASA Johnson Space Center, <sup>3</sup>University of Guelph, <sup>4</sup>Space Science Institute, <sup>5</sup>University of New Brunswick, <sup>6</sup>University of Western Ontario.

**Introduction:** Chemical signatures of weathering are evident in the Alpha Particle X-ray Spectrometer (APXS) datasets from Gusev Crater, Meridiani Planum, and Gale Crater. Comparisons across the landing sites show consistent patterns indicating silica retention and/or enrichment in open-system aqueous alteration.

**Spirit:** The Spirit rover at Gusev Crater traversed across 7.7 km over an operating lifetime of 2210 sols and analyzed with its APXS approximately 225 distinct targets. Fig. 1 depicts Mg/Si versus Al/Si for all the Gusev samples. A circular reference zone is plotted to represent an approximate average Mars crustal composition and the dashed lines bound the expected values for unaltered martian igneous rocks.



Fig 1: Molar Mg/Si versus Al/Si for APXS measurements at Gusev Crater. Red line shows trend of Si preservation and coupled Mg-Al depletion for many samples at Home Plate.

Basaltic soils and rocks from the Gusev plains plot within the zone of average crustal composition. However, many other samples show significant deviations from the average (see Fig. 1): (a) Weathered (Fe<sup>3+</sup>/Fe<sub>TOTAL</sub> > 0.7), possibly initially Mg-rich, Clovis class rocks [1], (b) high-Al, isochemically weathered Wishstone-Watchtower class rocks [1], (c) ultramafic, olivine-rich Algonquin class deposits [2], (d) Peace class ultramafic, magnetite-rich sandstones cemented by sulfates [1].

The lower left quadrant of Fig. 1 consists entirely of rock and soil samples analyzed in the vicinity of Home Plate, a ~90 meter diameter pyroclastic deposit. Extensive silica-rich deposits are found here, including soils with >90 wt% SiO<sub>2</sub>. Acid-sulfate weathering, consistent with the discovery of adjacent fumarolic deposits dominated by ferric sulfates, is likely responsible for leaching cations and leaving residual Si and Ti [3]. Direct precipitation from hydrothermal, Si-rich solutions may also be a contributor to these chemical signatures [4]. An open-system, chemical weathering environment was clearly once active in the Home Plate region.

Abundant water was present to mobilize elements from precursor materials. This process is in sharp contrast to other observations of aqueous weathering at Gusev Crater where there are only subtle chemical differences between altered samples and precursor rocks. The Wishstone-Watchtower alteration sequence, for example, likely occurred with a low ratio of water-torock, allowing only limited spatial redistribution of chemical constituents [1].

**Opportunity:** The Opportunity rover continues to operate at Meridiani Planum after over 40 km of traverse distance and nearly 3900 sols of surface operations. The Mg/Si versus Al/Si relationship for the ~400 APXS analyses is shown in Fig. 2.



Fig 2: Molar Mg/Si versus Al/Si for APXS measurements at Meridiani Planum.

Departures from the average composition depicted in the circular reference zone (Fig. 2) include: (a) The mafic erratic referred to as "Marquette Island," a likely impact ejecta block [5], (b) the aqueous precipitates and exceptionally high Mn coating "Island" rocks at the rim of Endeavour [6], (c) Al-smectite found as fracture fill ("Esperance") [7], and (d) Burns formation outcrop, where silica is a likely constituent [8].

The points representing apron deposits at the Endeavour Rim, referred to as "Grasberg" have low Mg/Si and Al/Si in Fig. 2, suggesting loss of Mg and Al and/or net gain of silica, perhaps by regional groundwater upwelling [9]. Acid-sulfate leaching processes may also contribute to the observed chemical signatures. Aqueous weathering in an open system and transport of soluble phases is further supported by the depletion of Mn relative to Fe in these samples.

**Curiosity:** The Curiosity rover continues to operate at Gale Crater after 10 km of traverse distance and 850 sols of surface operations. The Mg/Si versus Al/Si relationship for the ~180 APXS analyses is shown in Fig. 3.



Fig 3: Molar Mg/Si versus Al/Si for APXS measurements at Gale Crater.

Gale Crater soils fall within the zone for average martian crustal composition (circle in Fig. 3) and deviations along the approximately linear profile from high Mg/Si to high Al/Si are bounded by the high-Mg Windjana samples [10] and rocks of the Jake Matijevic class which have chemical compositions suggestive of a mugearite [11]. These samples within the dashed lines, including samples analyzed at Yellowknife Bay [12], have compositions comparable to pristine martian rocks and their Mg-Al-Si concentrations alone do not indicate a history of aqueous alteration.

The Stephen samples adjacent to Windjana, on the other hand, plot well outside the dashed lines and are exceptionally high in Mg, Mn, Cl, Ni and Zn. These materials may have formed as fracture-filling fluid precipitates. Also indicative of open-system weathering are samples that trend towards low Mg/Si and Al/Si. These analyses include Pahrump deposits at the base of Mount Sharp and the arguably related Bonanza King sample found ~300 m northeast of Pahrump. The pattern of lower Mg/Si in these samples suggests dissolution of mafic minerals and the removal of Mg<sup>2+</sup>. The similarity of the trend defined by the Pahrump and Bonanza King analyses in comparison to samples at Home Plate suggest that hydrothermal activity and/or acidsulfate leaching processes could be important at Gale Crater. The possibility of acid-sulfate weathering at the base of Mount Sharp is supported by the tentative initial detection of ferric sulfates such as jarosite in the CheMin x-ray diffraction data [13].

**Summary:** A consistent pattern of Al and Mg removal and relative enrichment of Si is evident at Gusev Crater, Meridiani Planum and Gale Crater. These chemical trends reflect open system weathering where cations are mobilized in fluids and the resulting composition differs significantly from that of the precursor materials. Similarities in the behavior of Mg/Si and Al/Si between Home Plate at Gusev Crater and Pahrump at Gale Crater suggest that hydrothermal alteration, possibly under acidic conditions, could be an important process in the formation of the deposits at the base of Mount Sharp.

**References:** [1] Ming D. W. et al. (2006) *JGR*, *111*, E02S12. [2] Ming D. W. et al. (2008) *JGR*, *113*, E12S39. [3] Squyres S. W. et al. (2008) *Science*, *320*, 1063-1067. [4] Ruff S. W. et al. (2011) *JGR*, *116*, E00F23. [5] Mittlefehldt D. W. et al. (2010) *41<sup>st</sup> LPSC*, #2373. [6] Arvidson R. E. et al. (2014) presented at 2014 Fall AGU. [7] Clark B. C. (2014) *45<sup>th</sup> LPSC*, #1419. [8] Clark B. C. (2005) *EPSL*, *240*, 73-94. [9] Ming D. W. et al (2015) *46<sup>th</sup> LPSC*. [10] Gellert R. et al. (2014) presented at 2014 Fall AGU. [11] Stolper E. M. et al. (2013) *Science*, *341*, #1239463. [12] McLennan et al. (2014) presented at 2014 Fall AGU.