

APXS CLASSIFICATION OF LOWER MOUNT SHARP BEDROCK: SILICA ENRICHMENT AND ACID ALTERATION. M. E. Schmidt¹, J.A. Berger², R. Gellert³, M.R.M. Izawa¹, D.W. Ming⁴, L. Thompson⁵, E. Desouza³, M. Fisk⁶, G. Perrett⁷ and the MSL APXS Team, ¹Brock U. (St Catharines, ON L2S3A1 Canada, mschmidt2@brocku.ca), ²Univ. W. Ontario (London, ON N6A 5B7 Canada), ³Univ. Guelph (Guelph, ON N1G2M7 Canada), ⁴NASA JSC (Houston, TX 77058), ⁵Univ New Brunswick (Fredericton, NB E3B5A3 Canada), ⁶Oregon St. U. (Corvallis, OR 97331), ⁷Cornell (Ithaca, NY 14850).

Introduction: Since landing in Gale Crater, the MSL Curiosity Rover has explored a lithologically diverse region of Mars [1, 2]. On sol 755, Curiosity began examining the first bedrock exposures attributed to the lower units of Mount Sharp, a 5 km-tall mountain of layered strata at the center of the crater. Sedimentary rocks of the Murray Fm. (mudstone, sandstone interbeds, and lesser conglomerate) and the overlying Stimson sandstone unit [3] generally exhibit a greater signal of open-system aqueous alteration than seen previously in the volcanoclastic Bradbury assemblage [4, 5]. We here summarize the rock classes examined by the MSL Alpha Particle X-ray Spectrometer (APXS) along the traverse of lower Mount Sharp.

Method: The MSL APXS measures abundances of major, minor, and some trace elements (Cr, Ni, Zn, Br, Ge) of ~1.7 cm spots on surfaces of rocks and soils [6]. Geochemical classes are identified as clusters of like analyses in element-element variation diagrams and named for the first, best described target (overnight integration, brushed or drilled) [7]. In some instances, related, yet distinct subclasses are also defined. To account for the S- and Cl-rich dust, all analyses are renormalized S- and Cl-free. Poor quality analyses (Fe FWHM >200 eV; a couple exceptions) and targets with obvious diagenetic features (veins or nodules) or that are very dusty are excluded from this treatment of the data. APXS classification complements a more general scheme based on texture and geochemistry [8].

Rock classes: We identify three new rock classes and four subclasses over sols 755 to 1200. In contrast to the Bradbury assemblage, which presents coherent arrays in elemental variation diagrams (e.g. Fig 1) linked to mixing of igneous components [2, 5], the new classes exhibit decreasing soluble element abundances (e.g., Mg, Al) relative to Si. APXS classes mostly follow stratigraphic units defined on the basis of grain size and sedimentary structures [3, 9].

The *Confidence Hills class* comprises mudstone to fine-grained sandstone ($n=12$) targets of the Murray Fm. Basaltic to basaltic andesitic in composition, its SiO_2 and Al_2O_3 contents are higher (ranging to 58.1 and 13.3 wt%, respectively) than mudstones examined earlier in the mission [1]. Concentrations of Zn and Ni are high at the base of Murray formation and generally decrease up section (e.g. 2631 to 751 ppm Zn). Diverse

diagenetic features (veins and nodules) are identified in associated targets [10].

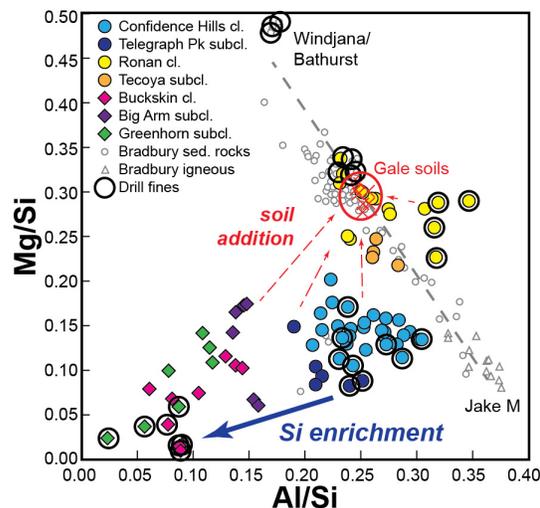


Fig 1. Plot of molar Mg/Si vs. Al/Si with APXS rock classes indicated. Dashed line represents mixing of igneous components among the Bradbury assemblage. Red arrows indicate contamination with local soils.

The *Telegraph Peak subclass* of the Confidence Hills class includes sandstone targets ($n=3$) examined near the top of the Murray Fm. It is characterized by lower abundances of Mg, Zn, Ni and higher Ti and Na than lower Murray rocks (Figs 1, 2A).

The *Ronan class* includes basaltic sandstone targets of the Stimson unit ($n=10$). Although it generally overlaps compositions of local soils in variation diagrams (Figs 1, 2A), it is more variable and ranges to higher Al and Si and lower Ti and Mn.

Basaltic sandstone targets of the Whale Rock outcrop ($n=3$) within the Murray Fm. are included in the *Tecoya subclass* of the Ronan class because they are more like Ronan class rocks than others in the Murray Fm. High CaO abundances (up to 14.2 wt%) among these targets are not associated with concomitant increases in SO_3 .

The *Buckskin class* includes two subclasses, which collectively encompass Si-rich bedrock targets. Buckskin class rocks are bedded and light-toned and found at the very top of the Murray Fm. Ranging to 79 wt% SiO_2 , Buckskin targets ($n=5$) are rich in Ti and S, low in Al, Fe, Ni, and Zn, and variable in P.

The *Big Arm subclass* includes Si-rich targets ($n=3$) found near the top of the Murray Fm., but are intermediate in composition to other Buckskin and Confidence Hills targets, implying mixing between materials of the two units, or a lesser degree of alteration.

The *Greenhorn subclass* targets ($n=5$) are associated with fractures cutting the Stimson unit. Relative to Buckskin, Greenhorn has higher Fe, Ca, and Cr, and lower Al, K, and Mn. Differences between these groups likely reflect differences between the precursor materials.

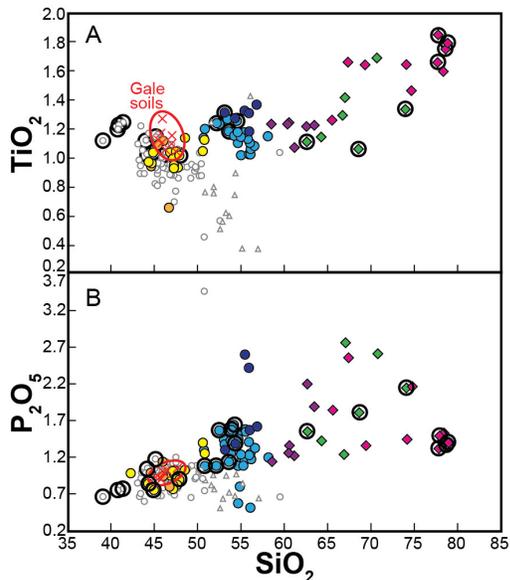


Fig 2. Plots of A: TiO_2 and B: P_2O_5 vs. SiO_2 (wt%) demonstrate enrichment in these elements relative to the Bradbury assemblage. Symbols as in Fig 1.

Discussion: APXS bedrock compositions of the Confidence Hills and Buckskin classes demonstrate clear SiO_2 enrichment trends (Fig 1) and are in agreement with the identification of jarosite in the Confidence Hills class samples and silica polymorphs and opal-A in Buckskin class samples by the CheMin instrument. Collectively, data from the two instruments support the interpretation of an episode of bedrock alteration by acid sulfate fluids [11-13].

In particular, a correlation between SiO_2 and TiO_2 (up to 1.85 wt% TiO_2 , a ~50% enrichment over soil or likely precursor materials) is strong indication of retention of immobile cations during interaction with acidic solutions. Si addition by near neutral fluids during cementation and diagenesis [14] cannot account for the high Ti contents, although such a process may have played a role in the diagenetic sequence. A ~90% depletion in trace metals Ni and Zn in the Buckskin class targets relative to likely precursor materials (Fig 3) is also not consistent with the 35-40% enrichment in SiO_2 if by Si addition alone. The soluble cations Ni

and Zn were more likely leached by late low pH fluids along fractures and low permeability layers. In addition, high and variable P among these rock classes (Fig 2B) suggest Fe-phosphate (as a crystalline or amorphous phase) precipitation from a solution loaded with dissolved solids under oxidizing acidic conditions [15], possibly very late in the sequence.

Early near isochemical alteration during diagenesis (cementation and lithification) is possible to account for the similarity in composition between the Ronan class rocks and average Mars soil [13]. CheMin found predominantly igneous minerals (plagioclase and pyroxene) in the Ronan class sample Big Sky [13], which is consistent with this rock type being relatively unaltered. However, lower Mn and Ni in Ronan class rocks suggest some degree of pervasive open-system modification if they are solidified soil.

Conclusion: APXS rock classification permits discussion of groups of rocks of similar composition. The open-system behavior indicated by Si enrichment and losses of more soluble elements point toward a widespread hydraulic system that interacted with basaltic sediments to create the observed geochemical diversity.

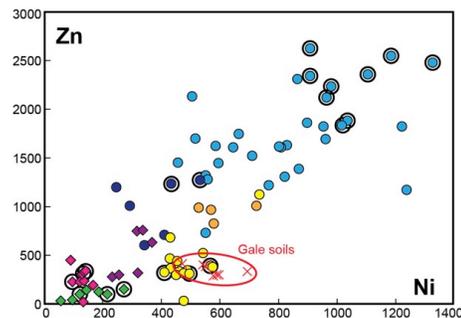


Fig 3. Plot of Zn vs. Ni (ppm). Symbols as in Fig 1.

References: [1] McLennan et al. (2013) *Science*, doi:10.1126/science.1244734. [2] Treiman et al. (in press) *JGR*. [3] Grotzinger et al. (2015) *Science* 350(6257). [4] McLennan et al. (2015) *LPS XXXXVI*, Abs# 2533. [5] Schmidt et al. (2014) *JGR* 119, 64-81. [6] Gellert et al. (this meeting). [7] Schmidt et al. (2014) *LPS XXXXV*, Abs# 1504. [8] Schmidt et al. (2015) *LPS XXXXVI*, Abs# 1566. [9] Milliken et al. (this meeting). [10] Berger et al. (2015) *AGU*, Abs# XX. [11] Rampe et al. (this meeting). [12] Morris et al. (this meeting). [13] Yen et al. (this meeting). [14] Hurowitz et al. (this meeting). [15] Berger et al. (this meeting).

Acknowledgements: The MSL APXS is managed and financed by the Canadian Space Agency, who also provided a Participating Scientist grant to Schmidt that supports Berger and Izawa.