TRACE ELEMENTS ON MARS: CHEMICAL EVIDENCE FOR AN AQUEOUS HISTORY AT GALE CRATER, MARS, AND OTHER LANDING SITES. R.Gellert[1], J.A.Berger[1], N.Boyd[1], E.D.Desouza[1], Catherine O'Connel-Cooper[2], L.Thompson[2], S.VanBommel[1], A.S.Yen[3]. [1]Univ. of Guelph (Guelph, ON, N1G2W1, Canada; rgellert@uoguelph.ca), [2]Univ. of New Brunswick, Fredericton, NB, [3]Jet Propulsion Lab, Pasadena, CA

Introduction: Three generations of the Alpha-Particle-X-ray-Spectrometer (APXS)[1] have been part of the science suite on all Mars rovers. For MSL and MER 16 standard elements are reported for all samples, including Ni, Zn and Br as trace elements with detection limits down to ~50-20 ppm, depending on integration time, standoff and overall composition. Here we report several additional trace elements that have been detected and quantified on MER and MSL. The discussion will focus on the Murray formation at Gale Crater from Pahrump Hills towards Vera Rubin Ridge(VRR), formerly known as Hematite Ridge, which the rover reached on sol 1780. The trace elements can be used for geochemical considerations, as well as distinguishing large scale rock formations and assessing their homogeneity and formation processes.

Method: The APXS measures x-ray emission after irradiation with x-rays and alpha particles. The sample diameter is ~2cm, x-rays are detected from the top ~5 µm for low z elements and up to ~100 µm for high z elements like the ones discussed in this work. Typical detection limits (DL) for a few hours of integration on MSL are: Ni, Cu, Zn, Ga, Ge, As, Se, Pb and Y ~15-40 ppm and Rb,Sr about 250 ppm. MER has slightly higher limits that require about 5 hours at least.

Germanium: The Murray formation at Gale crater is very consistently enriched with ~100 ppm Ge. Basaltic mudstones at Yellowknife Bay had similar values. Compared to soils, which were used to estimate the average Mars composition, this is about 10 times enrichment, likely through fluid activity [2]. Some samples around Homeplate at Gusev Crater had similar high abundances. Localized values of 600 ppm were found in the vein system at GardenCity, as well as in bedrocks at Meridiani Planum [3].

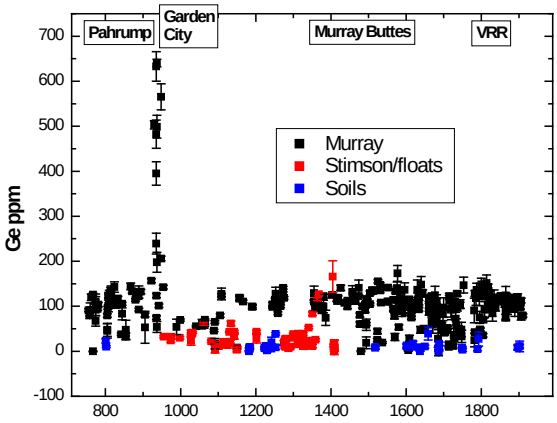

Figure 1 Germanium content at Gale. Colors indicate the different rock groups and soil as average Mars equivalent. Sol as x-axis represents the traverse as indicated by the location insets.

Manganese: MnO is one of the standard oxides quantified with good precision and accuracy. The ratio of Fe to Mn was found to be a versatile indicator for alteration of the igneous minerals originally containing both elements. Fe/Mn is consistently ~50 for soils/average Mars and for many unaltered rocks on MER and MSL. The Murray formation at Pahrump has an Fe/Mn of ~50, whereas significantly higher values dominate upsection. Just below the VRR, samples with very high MnO of up to 4% and P_2O_5 of up to 7.5% are found in an area of Fe/Mn of 50 and lower. Absolute values of MnO and FeO are besides the addition of $CaSO_4$ one of the few changes in the otherwise very homogeneous Murray composition.

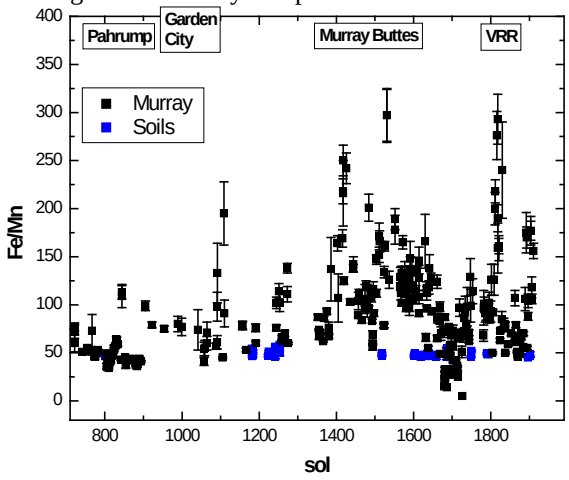

Figure 2 Fe over Mn ratio for the Murray formation

Lead and Selenium: Pahrump is highly enriched with up to 200 ppm Pb and 60 ppm Se. The upper regions of the Murray formation has lower but still consistently elevated values of 50 and 30 ppm, respectively. Values of average Mars, as measured in soils is at or below the DL of 15 ppm.

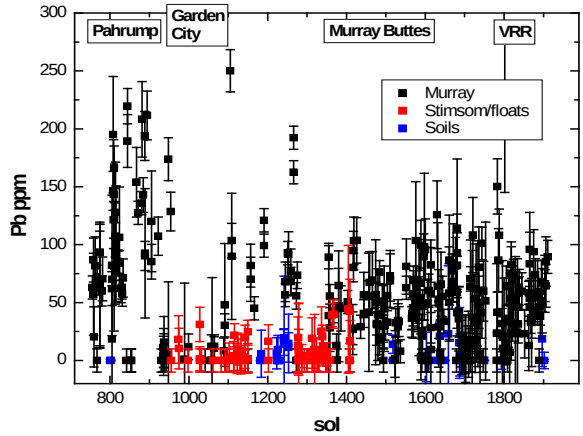

Figure 3 Lead at Gale crater. The Murray formation is consistently enriched with ~50ppm, compared to <20ppm in soils.

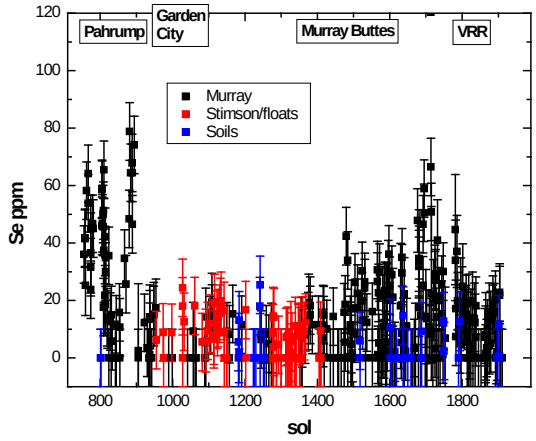

Figure 4 Selenium at Gale crater. Pahrump is highly enriched with ~50 ppm. Similar values are found localized just below the VRR, while a smaller enrichment might be present throughout Murray.

Elevated values of lead were also documented in the Wishstone rocks, felsic rocks with very high P and Ti in the Columbia Hills [4].

Other trace elements: Copper doesn't show any significant enrichment in the Murray formation over soil. However, it was found locally enriched in vein systems like Garden City, together with other metals like Mn, Ge and Zn, and in fracture fillings at Kimberley [5].

Strontium doesn't show any remarkable trends, except the absence of any enrichment in the $CaSO_4$ veins. On the other hand, at Merdiani Planum, the vein Gascon-ade, measured ~sol 4500, shows two of four spots enriched with ~3000ppm Sr. At Gale, one sample, Kern-peak, an altered rock immediately adjacent to the Garden City veins, shows 700ppm Sr, accompanied by 140ppm Ga, high Pb and P, with very low Ca.

Bromine is an easy mobilized, salt-forming element. With similar solubility as Chlorine, the Cl to Br ratio for soil is close to the meteoritic CI value of 270 or lower with very small abundance of both elements. Almost all of Murray is significantly lower, indicating a Br enrichment. Very recent samples at VRR show a relative Chlorine enrichment.

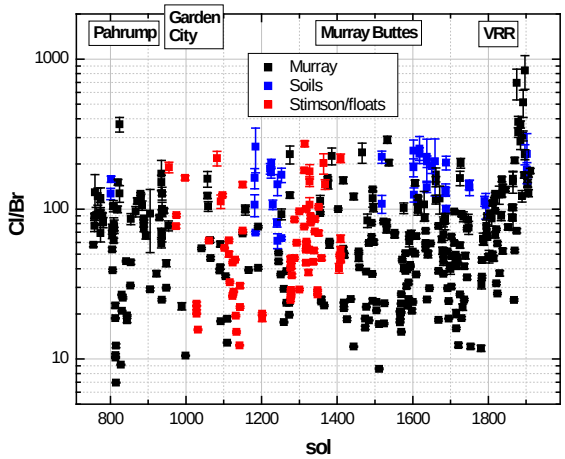

Figure 5 *Cl/Br at Gale crater. Bromine values go up to several 1000s ppm and Chlorine reaches over 3%*

Summary: Trace elements help to separate distinct rock groups and provide evidence for their possible formation and alteration processes. The Murray fm values for Ge, Pb, and Se represent 50 to 1000 times enrichments relative to Martian crust predictions [6]. Co-enrichment of these elements at such concentrations is a possible fingerprint of hydrothermal activity.

The overall chemical homogeneity of the extensive Murray formation is a remarkable finding of the MSL mission, especially since Murray includes the VRR that shows evidence for hematite from orbit. While local modifications like the $CaSO_4$ veins or the high silica halos are evident, the overall pattern of low Mg and Ca vs average Mars can be followed over kilometers [6].

The very consistent Ge enrichment is one of the clear distinguishing points to other materials like the average Mars like Stimson formation and soil. The varying abundance of hematite in the Murray formation, as determined by ChemMin [8] might be connected to the varying Fe/Mn ratio [6]. Fig 6 shows that Murray is slightly enriched in Si over average Mars, but not enriched in Fe. However, there are samples with clear Fe enrichment, indicating mobilization of Fe and precipitation as, possibly, hematite.

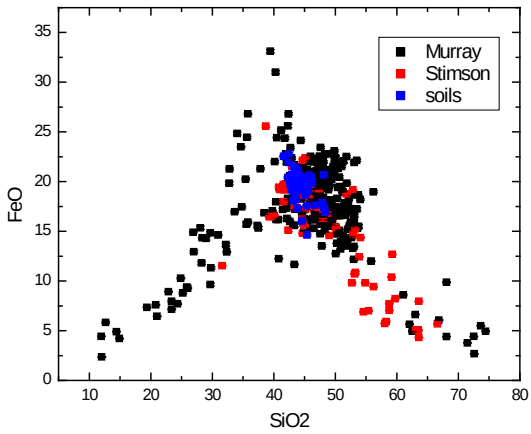

Figure 6 *Si vs Fe at Gale crater. The lower left corner represents CaSO4 veins, the high Si values are the alteration halos in Murray and Stimson.*

References: [1] Gellert, Clark (2015), Elements [2] Berger, JGR, 2017, [3] Mittlefehldt, (2016) 47th LPSC, #2086, [4] Gellert et al (2006) JGR Planets Vol 111, JE002555, [5] Lanza et al., (2016) GRL, 43, 7398–407, [6] Lodders and Fegley 1997, [7] Thompson et al, this conference, [8] Rampe, E. B., et al., (2017) *48th LPSC*,#2821.

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