

RECENT SODIUM AND CHLORINE ENRICHMENTS IN THE MOUNT SHARP GROUP IN GALE CRATER, MARS. R.Gellert¹, J.A.Berger², N.I.Boyd¹, C.D.O'Connell-Cooper³, M.A.McCraig¹, L.M.Thompson³, S.J.VanBommel⁴, A.S.Yen⁵. ¹University of Guelph (Guelph, ON, N1G2W1, Canada; rgellert@uoguelph.ca), ²Johnson Space Center, Houston, TX, ³University of New Brunswick, Fredericton, NB, ⁴Washington University in St. Louis, St. Louis, MO, ⁵Jet Propulsion Lab, Pasadena, CA

Introduction: Chlorine and sulfur are omnipresent on the surface of Mars, as attested by the x-ray spectroscopy measurements of all Martian rovers, e.g.[1]. Correlations of S and Cl abundance in soils and an enhanced concentration of these elements in the fine-grained Martian dust indicate that these elements are likely the result of local rock alteration that later was abraded and globally transported by wind and likely further reacted locally with rocks and fluids.

In the past, much attention has been paid to perchlorates and their detection or production processes; however, their lack of definitive detections compared to the typically >0.5% Cl abundance from the APXS leaves a lot to learn about the chlorine history on Mars. Here, we report the recent detection of >10% Cl enrichment in the Mount Sharp Group, encountered during the transition from the clay-bearing unit into the presumed sulfate region in Gale Crater.

Method and Findings: The APXS, e.g.[2], is an arm-mounted X-ray spectrometer using a combination of PIXE and XRF to quantify 16 standard elements, among them S, Cl and Br, with high precision, good accuracy and low detection limits. It measures a sample of approximately 2cm diameter at depths given by the typical escape range of the characteristic x-rays, ranging from a few μm for Na to $\sim 100\mu\text{m}$ for Br.

Along the $\sim 25\text{km}$ uphill traverse of Curiosity, the APXS was used to document the composition of the bedrock every $\sim 5\text{m}$ elevation gain. On sol 3183, the target Montagenet, fig.1, a short 20 minute T&G integration in the same workspace as the Pontours drill target, showed a

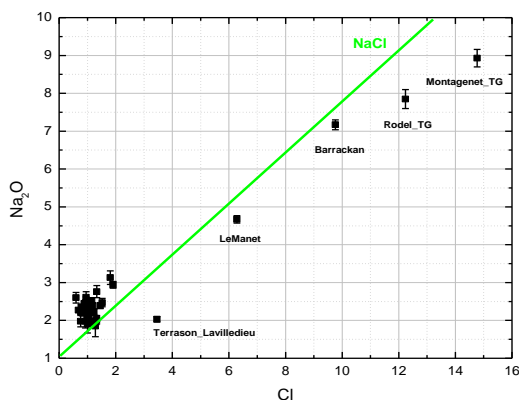


Fig. 1: Na vs Cl for recent bedrock targets

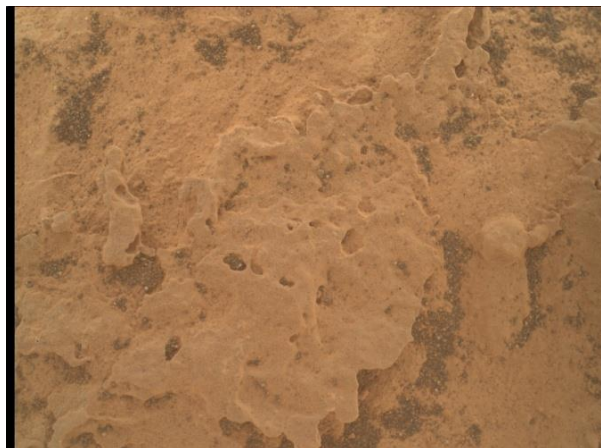


Fig 2: MAHLI of Montagenet, credit MSSS/JPL

record breaking $\sim 15\%$ chlorine abundance, accompanied by highly elevated sodium. Over the next 20 sols, similar samples were found within a few 100 meters and 10 meter elevation gain, fig.1.

Na,Cl spatial distribution over APXS FOV:

The MAHLI image of Montagenet, fig.2, shows that there are no obvious $\sim \text{mm}$ sized crystals that could be pure, macroscopic Na,Cl grains that partially fill the APXS FOV. Additionally, ChemCam MOC data of the neighboring sample Montagrier show in 4 out of 6 of their $\sim 0.5\text{mm}$ diameter spots similarly elevated Na (Cl is not reported). This indicates that the Na,Cl phase is present in clearly sub mm grains and/or as a cryptocrystalline coating or matrix. All four of the high Cl targets have no other APXS detectable elements correlated with Cl other than Na, fig.2. The logarithmic ratio to the drill hole sample Pontours indicates that only Na and Cl seem to be added to the typical bedrock in this region in a couple of spots (fig. 3).

Discussion of the possible Na,Cl phases: While chemistry alone cannot provide definitive mineralogy, in this case a discussion of possible minerals is beneficial, since for Na and Cl abundances the grain composition significantly impacts the extracted APXS values. From fig.1, one could conclude that Na and Cl have roughly a 1:1 molar ratio, with Na being a bit lower due to a thin dust cover that is lowering the Na signal by a few 10 percents. However, as discussed in the MER APXS calibration paper [3] – and often ignored in spreadsheet mass-balance exercises – the extracted elemental concentrations assume a homogeneous composition to

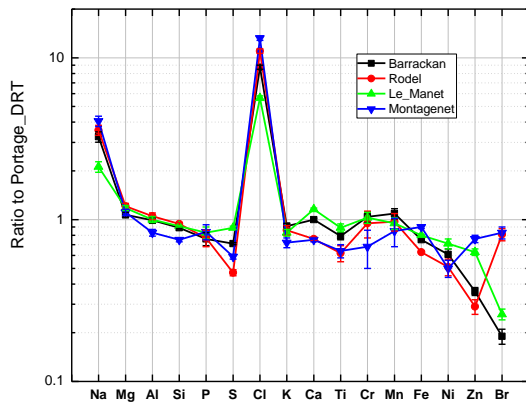


Fig.3: Ratio to Pontour bedrock

correct for self-absorption. This accounts for the large accuracy estimate of 30% for Cl. While this can be often a minor effect (e.g. for CaSO_4 , where both APXS detected elements have similar energies, resulting in the very consistent ~1:1 APXS molar ratio of Ca to S in Gale Crater due to Calcium sulfate veins), halite is actually a very different case. Key is the missing oxygen in this mineral, impacting the signal detected for Na and Cl. NaCl (40% Na by weight) measured in the lab has a Cl to Na peak ratio of ~1.5, while the high Na,Cl spectra on Mars have around 4 and higher. This could either indicate that the dust cover is significantly higher than estimated from fig.1, or that the NaCl grains are of sub-micrometer size and finely intermingled with average rock that resembles a homogeneous sample, the assumptions made in the APXS analysis.

NaClO_4 (19% Na, 52% O by weight) would resemble the average rock composition as well and make extracted Na,Cl abundances from fig.1 realistic. However, then the ~20% NaCl would come with ~20% excess oxygen. This excess ALIC [4] (additional light invisible component) amount should be detectable in the scatter peaks of the APXS spectra. None of the spectra indicate any excess oxygen, making perchlorates unlikely. Sub-micrometer grains would also be consistent with fine NaCl coatings of grains, possibly a model also applicable for the fine Martian dust.

Discussion: The recent encounter of highly elevated Na and Cl seems locally limited in the stratigraphy of Mount Sharp and has not been observed at any other landing site in this magnitude. It occurs as slightly darker (than the surrounding bedrock) surface coatings along sub-horizontal surfaces that may be exposed veins. The interpretation of the APXS Na and Cl values in this case depends on the actual form it occurs in.

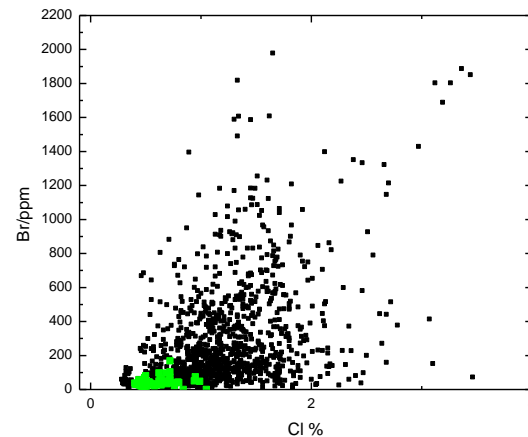


Fig.4: Cl and Br in Gale Crater, with soils in green.

Results are most consistent with a sub-micrometer addition of NaCl compounds. Perchlorate is inconsistent with the missing increase in oxygen in the APXS scatter peaks. It emphasizes once again how results from any instrument should honestly discuss the caveats of their method to avoid misinterpretation of the data.

In any case, this finding is another reminder that Cl and Br played a significant role in the alteration history of Mars, as can be seen in fig.4. Br and Cl are strongly enriched over their soil values, which represent an average Mars composition. The soil Cl/Br ratio is in the order of the Cl value of 270, further solidifying that the soil is representing the abraded and globally distributed surface composition of Mars, including alteration products of large scale events that produced the sulfur enriched Burns formation and likely halogen enriched formations. The large local enrichments of Cl and Br, even in cm deep drill holes, have been caused by their different solubility for later local fluid events.

High Cl and Br are often correlated with elevated Fe (like TerrasonLavilledieue in fig.1 with ~40%FeO) or high Mn and Mg (Stephen). Future findings, hopefully in drill samples or multiple spot APXS rasters, will allow further insights.

References: [1] Gellert et al, 2004, Science, Vol 305, [2] Gellert, Clark,(2015) Elements,11(1), [3] Gellert et al, (2006),JGR Vol111, JE00255, [4] Campbell et al, 2008,JGR,Vol 113,E6. All data use are available on the PDS,<https://pds-geosciences.wustl.edu/missions/msl/>

Acknowledgements: The MSL APXS is managed and financed by the Canadian Space Agency, with MDA as prime contractor to build the instrument.Science team funding is provided by CSA.