Carbonate Minerals at Gale Crater: Using LIBS to Assess a Warmer Past TRUST Martian Climate

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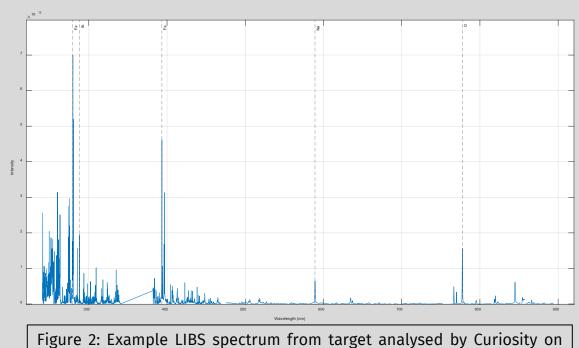
Curiosity at Gale Crater

Curiosity has been operating since 2012, traversing from the clay-rich crater floor up Gale Craters' central peak, Mount Sharp. Throughout this journey, many observations have confirmed the presence of past liquid water at the site throughout various points in history. Given these past aqueous conditions, as well as the planets' basaltic bedrock, we should expect Gale Crater to be an environment rich in carbonate minerals. However, Curiosity has thus far reported only a few small-scale carbonate deposits and orbital observations (Fig 1) show a similarly sparse carbonate environment⁽¹⁾. We seek to offer a widescale overview of the carbonate environment across Gale using data from Curiosity's entire mission.

Figure 1: Carbonate identification bands across Gale Crater from orbital CRISM analysis, Curiosity's route marked in blue.

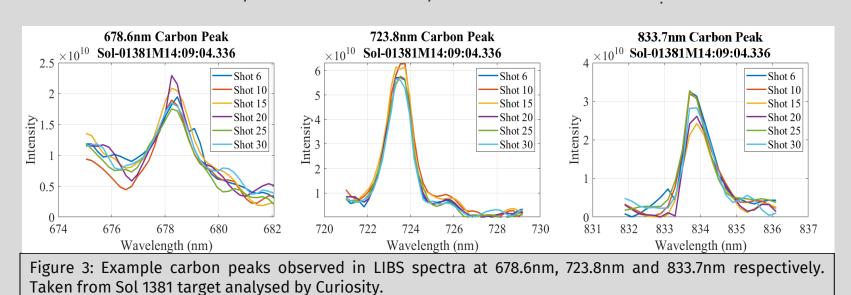
Laser Induced Breakdown Spectrometry

Curiosity operates a laser induced breakdown spectrometry (LIBS) unit. This is a remote detection device capable of analysing targets up to 7m away. As a result, Curiosity can provide LIBS analysis of multiple targets per mission Sol meaning we have a very large database from over 3500 Sols to work with, covering a range of elevations up Mount Sharp. Major peaks are observed for many elements such as Fe, Si and Na (Fig 2) in LIBS.



When using LIBS to search for carbonate minerals there are three minor carbon peaks suitable for identification, visible at 678.6nm, 723.8nm and 833.7nm⁽²⁾

Sol 1500, major peaks indicative of Fe, Na, Si and O labelled.



LIBS analysis typically operates a 30-shot process. When a target is selected, each point on a target has 30 laser shots fired at it, causing a slight penetration into the material. Spectral data from these 30 shots can be analysed individually or as a mean, the first 5 shots are generally discarded due to dust. As targets are sampled from a range of distances, insufficient laser coupling can become an issue. To account for this the total spectrum energy is calculated for each shot and a threshold limit is set.

We use data from Sols 0-3423, dividing our analysis into 100 Sol sections. Separating into Sol sections allows for an ease of processing and accounts for any seasonal variations. The database we work with here consists of 24,271 total LIBS spectra.

Calcium Sulphate Check

In total, we report seven LIBS analysis points rich in both calcium and carbon and indicative of calcium carbonate minerals. A final consideration we must make before determining these minerals to be calcium carbonate, is the possibility of calcium sulphate. Calcium sulphate is present within Gale Crater, specifically units are sulphate rich at elevations above the crater floor. Given this, we assess sulphur peak intensity in all carbon/calcium rich targets. We compare this sulphur signal with that of previously assessed targets in Gale.

All seven carbon/calcium rich targets display a sulphur peak of some intensity. However, given the high enrichment of calcium present we find that calcium sulphate is not a viable explanation for calcium present in targets identified on Sols 1248, 1707 and 2576.

Given the clear carbon/calcium enrichment in all seven of these points, we suggest these may be representative of a caliche like mineral, where calcium carbonate and sulphate are each present.

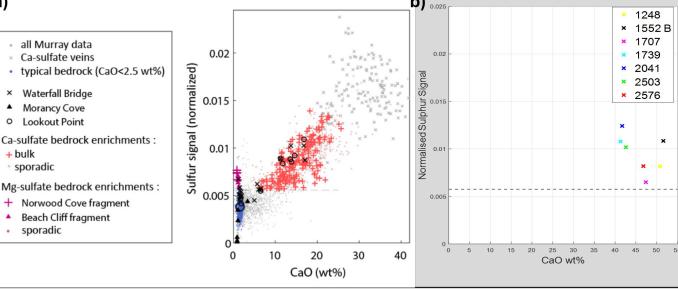


Figure 6: (a) Sulphur peak intensity for various LIBS analysis points throughout Gale Crater (b) comparative sulphur peak intensity for 7 carbon/calcium rich targets identified in this study.

Calcium Carbonate Minerals

Here we present Remote Micro-Imager (RMI) close-up pictures for two calcium carbonate minerals identified (Fig 7). We also show colour images of other carbon/calcium rich targets. Visually we see all seven of the carbon/calcium rich targets are composed of lighter toned material in comparison to surrounding bedrock.

In the case of all seven carbon/calcium rich minerals, we see the area analysed is composed of a similar lighter toned material.

In both context images presented here, we observe the lighter material as a minor occurrence among the surrounding bedrock. In total, we can only conclusively report on 3 carbonate minerals within the 24,271 total spectra analysed.

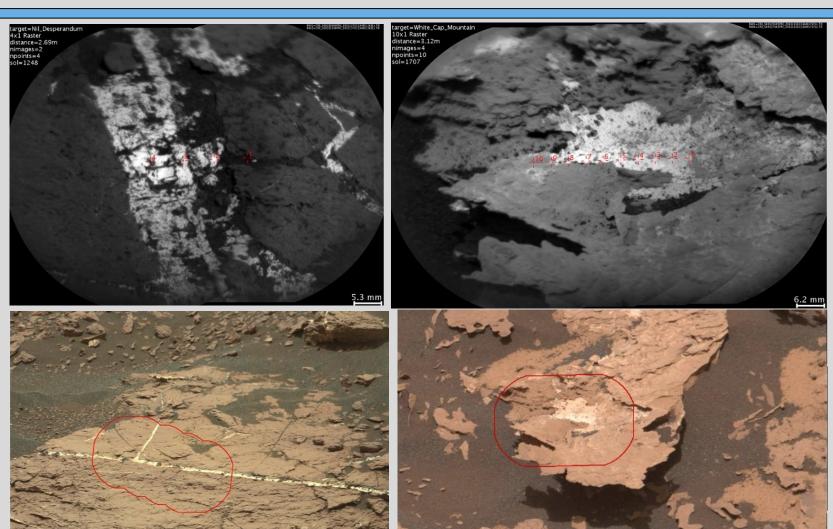


Figure 7: RMI images of targets analysed by LIBS on Sols 1248, 1707, 1552 and 1707 respectively.

A Climate Paradox

Results presented here further outline Gale Crater as a paleolake lacking ubiquitous large scale carbonate deposits. Nearly all climate models require a dense, CO₂ rich past atmosphere to allow for liquid water to remain stable on Mars' surface, given the basaltic nature of Mars we should expect to see carbonate formation occur readily at sites such as Gale. However, our results not only show very low number of small-scale deposits, but we also see no carbonates present in the crater floor where liquid water would have persisted for the longest period of time.

These results are somewhat reminiscent of carbonates identified within the crater rim at Jezero crater⁽⁵⁾ (another Martian paleolake). We have now seen two separate sites at which carbonates are absent from ancient lake beds however do persist as small-scale deposits elevated from the crater floor.

The Silicate/Carbonate weathering cycle may explain these discoveries. With multiple aqueous periods occurring in Mars' past, the timescales of these events may have led to carbonate formation then later weathering leaving the surface we see today.

Results here directly lead into future work, assessing periods of carbonate weathering within transient wet periods

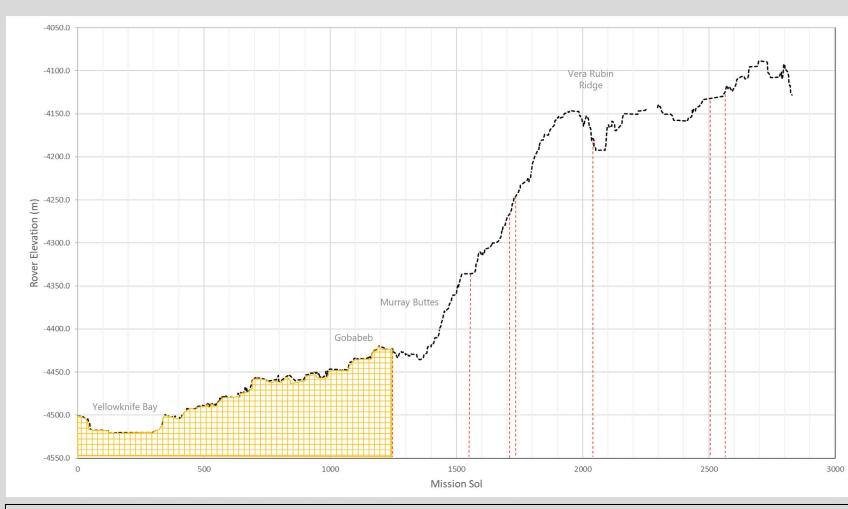


Figure 8: Elevation of all carbon/calcium rich targets identified in Gale Crater marked in red, absence of carbonate minerals within crater floor noted in yellow.

on the Martian surface.

Atmospheric Carbon Deviation

Due to the enriched CO₂ atmosphere present when operating LIBS analysis on Mars, all targets display a carbon peak in their spectrum. To differentiate atmospheric carbon from that of carbon containing minerals we normalise our data using an oxygen triplet also observed in LIBS spectra (Fig 4).

By plotting average intensity values of four carbon peaks against intensity values of three oxygen peaks, we establish an atmospheric trend line for each 100 Sol section and can determine which targets show an actual appreciable level of carbon.

Quantifying high carbon targets is done so via calculation of a 'C-Score' as

$$C Score = \frac{\Delta C}{\sigma}$$

where ΔC is the x-distance a point plots from the atmospheric trend line and σ is the standard deviation of all ΔC in a 100 Sol section.

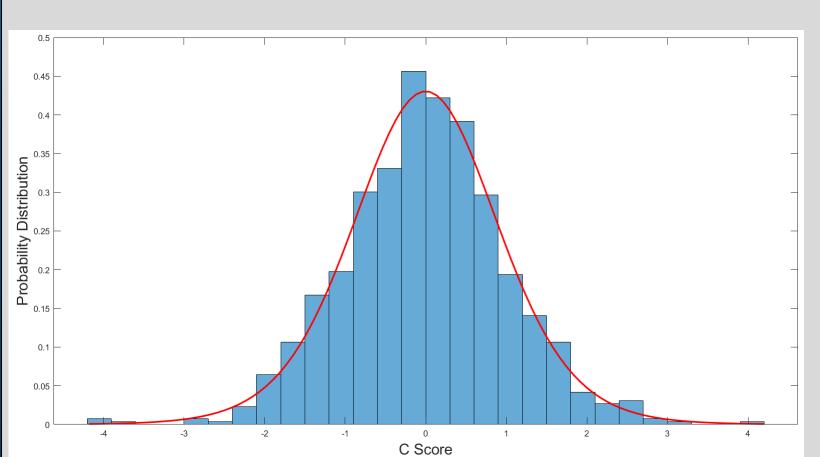


Figure 5: Students distribution of C-Score values between Sols 1700-1800.

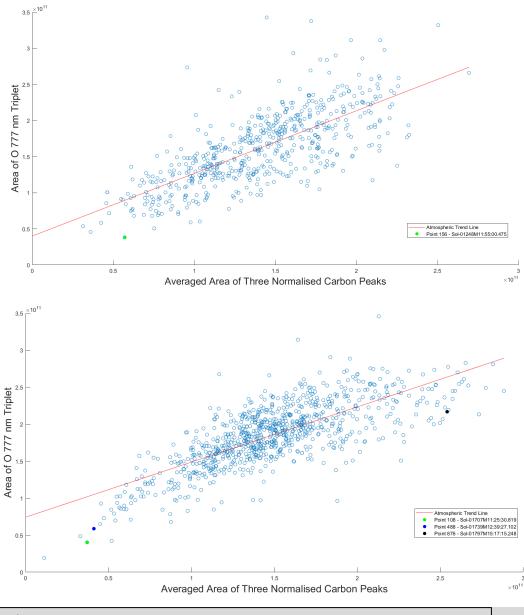


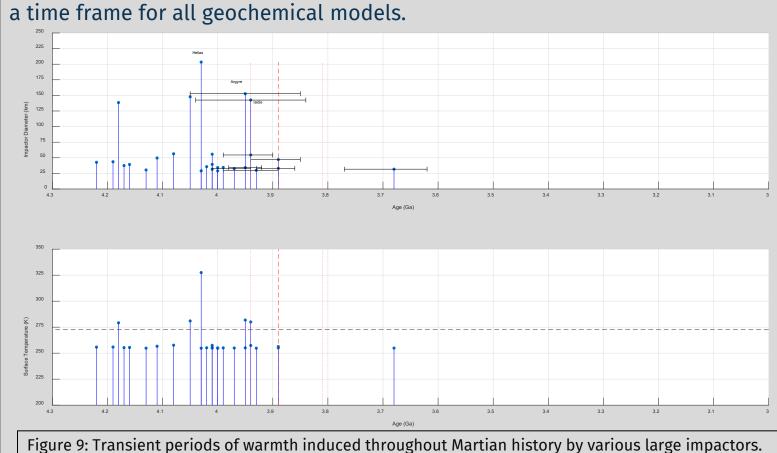
Figure 4: Carbon-Oxygen plot for all targets analysed between Sols 1200-1300 and 1700-1800 respectively, atmospheric trend line and high carbon targets plotted.

C-Score values are fit to a Students distribution (Fig 5). When this distribution is centred at zero, targets that plot above 1.28 standard deviation are considered high carbon minerals and potential carbonates⁽³⁾.

From this process we have identified carbon containing targets, therefore potential carbonate minerals. More analysis is needed of these carbon containing minerals to identify carbonates within Gale Crater.

Future Work

Assessing carbonate weathering in the Hesperian era (3.7-2.5 Gya) is crucial to rationalise the carbonate environment present on the surface today. My future work will involve geochemical modelling of lightly acidic solutions in Martian analogous environments. Modelling will consist of transient warm periods induced by the impact of various meteorites throughout Martian history. Large enough impacts release H₂ gas into the atmosphere, triggering an enhanced greenhouse effect and with that, raised temperatures. These warm periods are transient due to instability of hydrogen in the Martian atmosphere, thus give us



References

- Bridges, J.C., Hicks, L.J. and Treiman, A.H., 2019. Carbonates on mars. In Volatiles in the Martian crust (pp.
- Anderson, D.E., Ehlmann, B.L., Forni, O., Clegg, S.M., Cousin, A., Thomas, N.H., Lasue, J., Delapp, D.M., McInroy, R.E., Gasnault, O. and Dyar, M.D., 2017. Characterization of LIBS emission lines for the identification of chlorides, carbonates, and sulfates in salt/basalt mixtures for the application to MSL ChemCam data. Journal of Geophysical Research: Planets, 122(4), pp.744-770.
- Clavé, E., Benzerara, K., Meslin, P.Y., Forni, O., Royer, C., Mandon, L., Beck, P., Quantin-Nataf, C., Beyssac, O., Cousin, A. and Bousquet, B., 2023. Carbonate detection with SuperCam in igneous rocks on the floor of Jezero Crater, Mars. Journal of Geophysical Research: Planets, 128(6), p.e2022JE007463. Anderson, R.B., Forni, O., Cousin, A., Wiens, R.C., Clegg, S.M., Frydenvang, J., Gabriel, T.S., Ollila, A., Schröder,
- S., Beyssac, O. and Gibbons, E., 2022. Post-landing major element quantification using SuperCam laser induced breakdown spectroscopy. Spectrochimica Acta Part B: Atomic Spectroscopy, 188, p.106347. Zastrow, A.M. and Glotch, T.D., 2021. Distinct carbonate lithologies in Jezero crater, Mars. Geophysical Research Letters, 48(9), p.e2020GL092365.