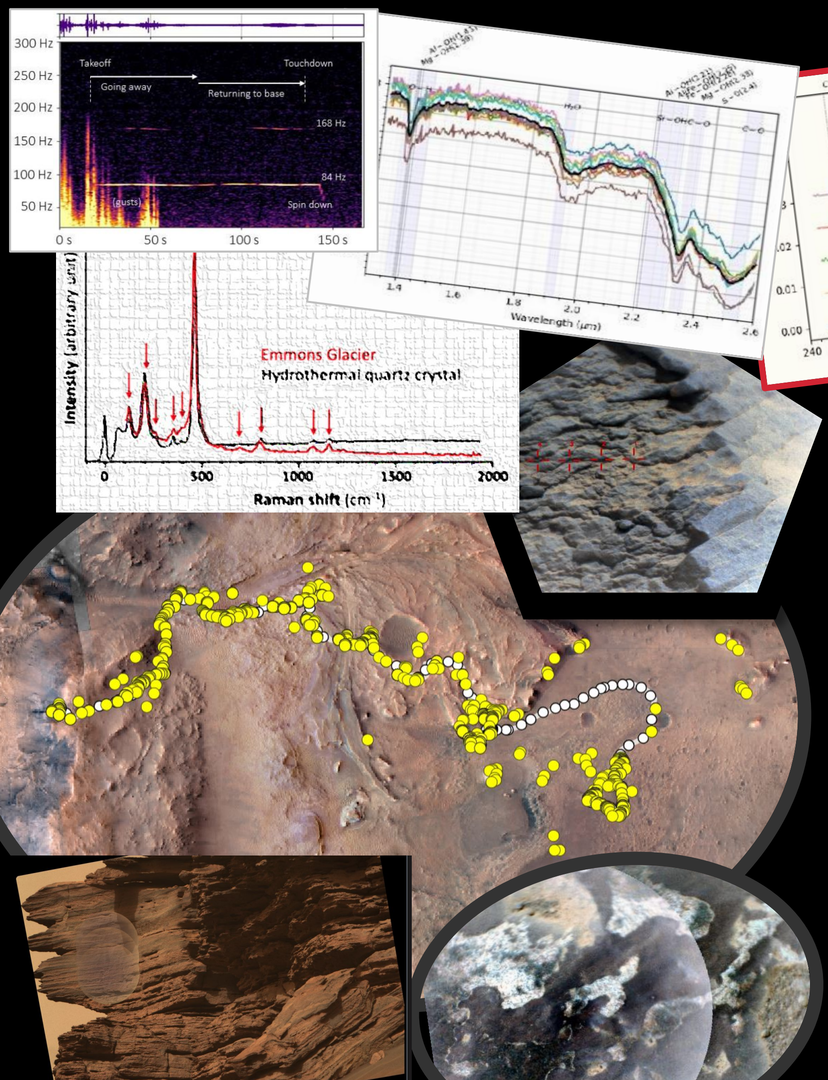

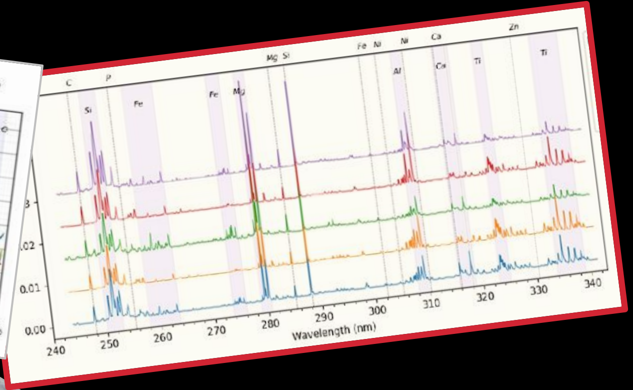

Mars 2020 Project
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LIBS Spectroscopy
- Elemental Chemistry -

Agnes Cousin on behalf of the LIBS WG

SuperCam Data Workshop

LPSC, The Woodlands, Texas, USA
Tuesday, March 11, 2025

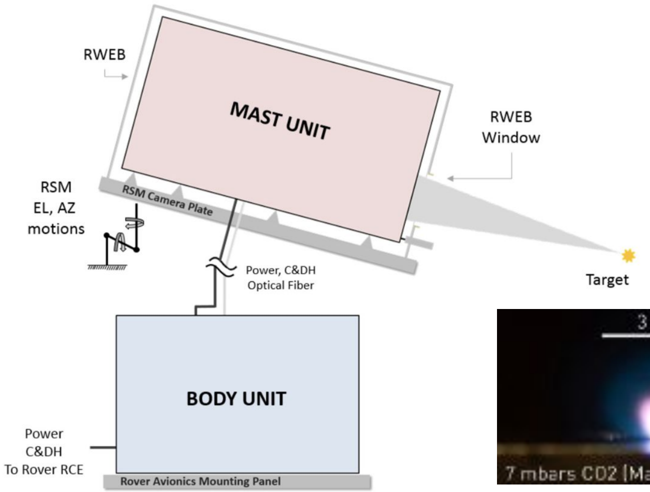
MARS 2020 SUPERCAM

Outline

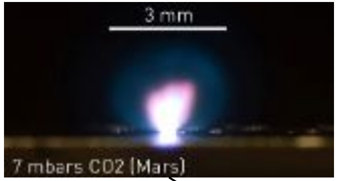
- LIBS technique overview
- SuperCam LIBS instrument details
- LIBS processing
- Major Element Oxide (MOC): Quantification
- Next Steps
- PDS release process
- List of papers and useful tools

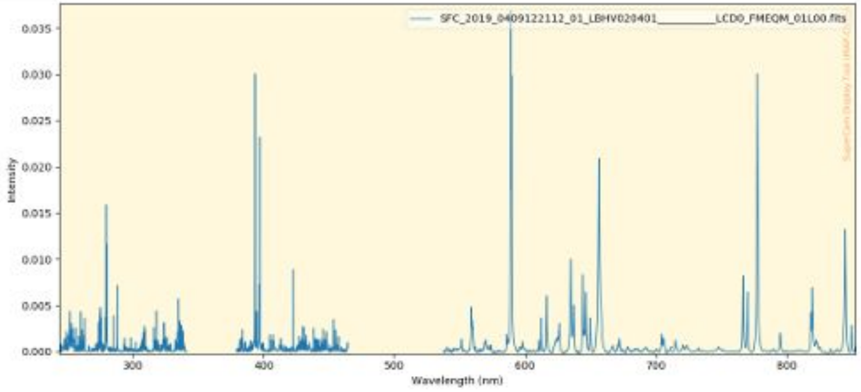
LIBS technique overview

- Remote sensing technique: >10 m
- Spot size: 100-450 microns (between 1.5 - 7m)
- From UV to near Infrared (243.5 - 853 nm)
- Different raster types (see introduction)
- Depth profiles are possible (up to 500 shots)
- Advantages:
  - Quick, no sample preparation
  - Remote sensing (no arm placement)
  - Acquires ample of data

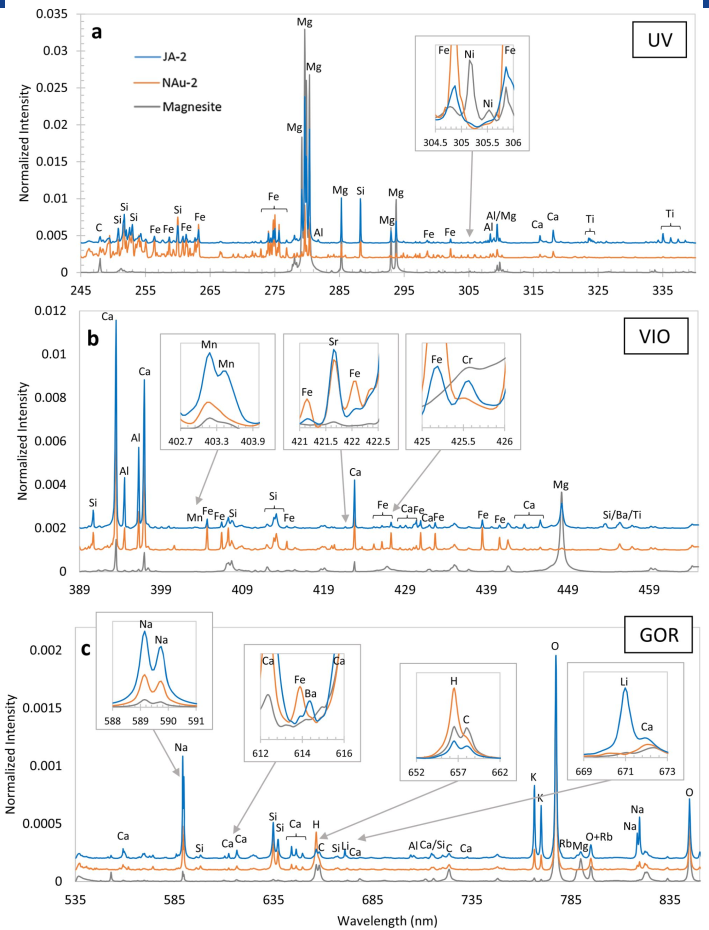


Maurice et al., SSR, 2021
Wiens et al., SSR, 2021





SuperCam LIBS instrument details



- Three spectrometers (range, resolution):
  - UV: 243.5 - 341.7 nm, 0.05 nm/pixel
  - VIO: 382.1 - 467.5 nm, 0.04 nm/pixel
  - Transmission spectrometer - 0.06 - 0.09 nm/pixel
    - Green: 535 - 620 nm
    - Orange: 620 - 712 nm
    - Red: 712 - 853 nm

- Major elements that are quantified:
  - Si, Ti, Al, Fe, Mg, Ca, Na and K
- Minor elements that can be observed:
  - Rb, Ba, Sr, Mn, Cr, Li, Ni, Cl => quantification in progress
  - Cu, S, F, P, N, C, H, …

LIBS processing

- Raw data need to be processed (noise & background removal, radiance correction,..)
  - These steps are presented in Wiens et al., 2021 and in Anderson et al., 2022

- LIBS Quantification is challenging
  - Distance is varying
  - The physics of the plasma are challenging and cannot be modeled well enough for an accurate "first principles" quantification
    - Rapidly changing plasma (temp, density, opacity, shot to shot interactions, ..)
    - Atoms and molecules in the plasma interact with each other – **"Matrix effects"**
      - Intensity of emission from one element can change due to concentrations of other elements
  - Empirical calibration based on laboratory data for which we have independent compositions (our "LIBS database")
  - Use of average spectra for a better SNR

- Multivariate vs Univariate approach:
  - Univariate:
    - Single variable
    - Simple and easy to interpret
    - Do not perform as well as multivariate tools for major elements
    - Matrix effects are not accounted for
  - Multivariate:
    - Use several variables (whole spectra, or many spectral channels)
    - Mitigate better than univariate approach the matrix effects
    - Can be difficult to interpret

We have developed multivariate models for our quantifications

Major Element Oxides (MOC) - Anderson et al., 2022

- Details about setup, database (334 samples) pre-processing are in Anderson et al., 2022
- 11 regression algorithms have been tested
- For some elements, the combination of different models were giving the best results, as well as some blended models
- Accuracy is determined by Root Mean Square Error of Prediction (RMSEP)

Element	RMSEP wt%	Model
SiO_2	6.1	Average (GBR, PLS)
TiO_2	0.3	RF
Al_2O_3	1.8	Average
FeO_T	3.1	GBR
MgO	1.1	GBR
CaO	1.3	Blend RF + PLS
Na_2O	0.5	Blend GBR + LASSO
K_2O	0.6	LASSO

- Precision (shot-to-shot standard deviation) is always better than accuracy

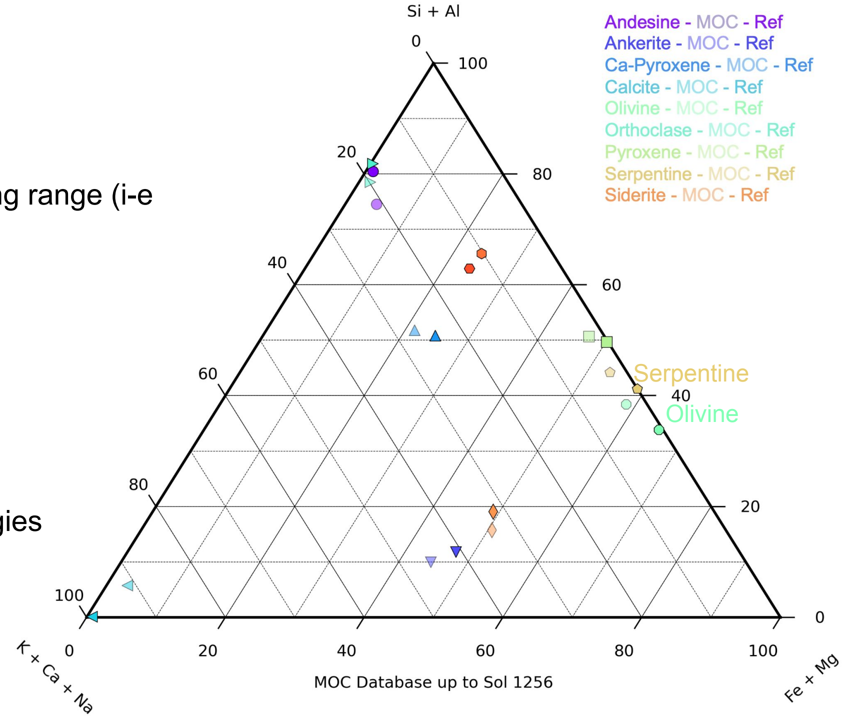
	SiO_2	TiO_2	Al_2O_3	FeO_T	MgO	CaO	Na_2O	K_2O
3 m Test Set (Laboratory)	0.8	0.06	0.4	0.5	0.2	0.2	0.1	0.1
SCCTs (Mars)	1.6	0.02	0.7	1.3	0.5 (0.3)	0.5	0.3 (0.2)	0.3

- This is the first quantification effort was made a few months only after the landing, with known idiosyncrasies

Major Element Oxides (MOC) - Anderson et al., 2022

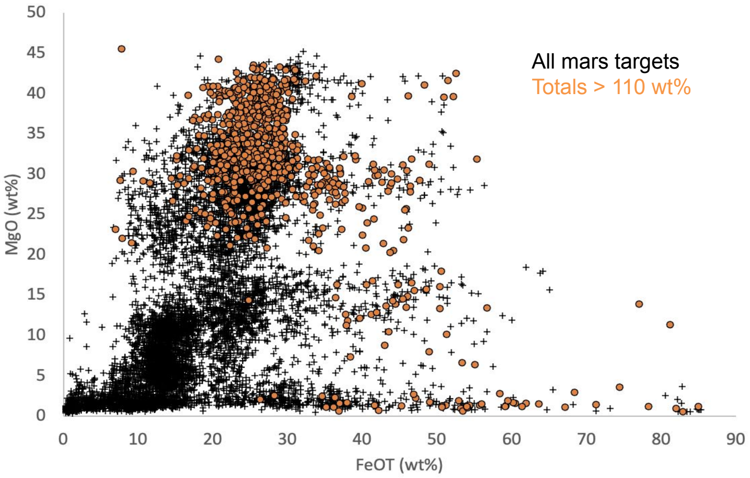
Some idiosyncrasies about the MOC

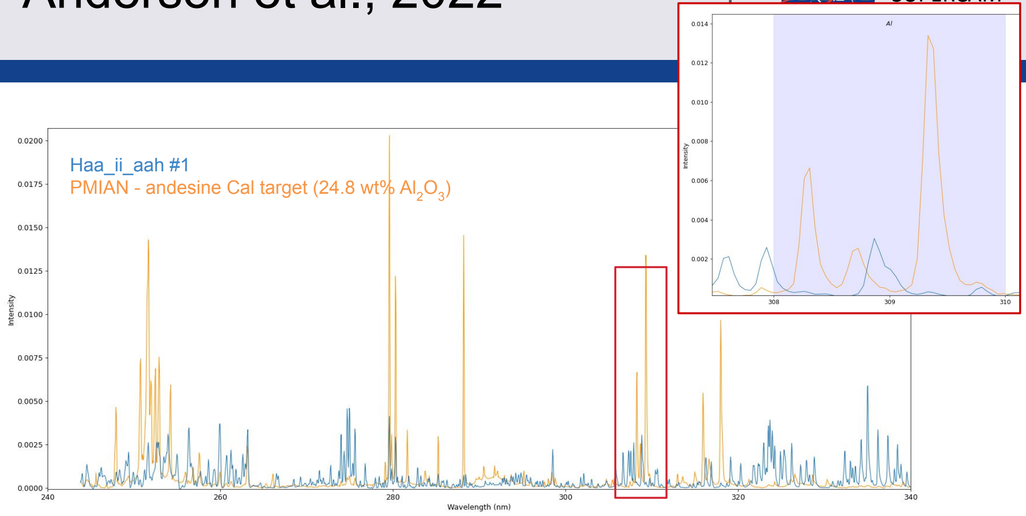
- SiO2:
    - Overestimated for olivine mineralogies
    - Poor discrimination for some minerals between 40-60 wt%
- TiO2:
    - Model (Random Forest) not able to extrapolate outside the training range (i-e 3.4 wt%) => high contents are underestimated
- Al2O3:
    - Suffers some matrix effects - overpredicted when Ti is elevated
    - Overpredicted at low contents
- FeOT:
    - Underpredicted for mars dust
    - Seems to be underestimated in olivine mineralogies
- MgO:
    - Bimodality/Quantized predictions, not always related to mineralogies
    - Highest predictions are related to sum of oxides >100 %.
- CaO:
    - Bimodality in the predictions
- Na2O:
    - No issues that we are aware of !
- K2O:
    - LIBS is very sensitive to K lines.



Major Element Oxides (MOC) - Anderson et al., 2022

Some idiosyncrasies about the MOC





target_name	point	SiO2	TiO2	Al2O3	FeOT	MgO	CaO	Na2O	K2O	Total
Haa_ii_aah	1	20,4	2,62	17,41	22,68	2,43	5,25	1,61	1,96	74,36

- Even though our actual LIBS quantification has known caveats, MOC is actually very good.
- Very good precision: easy to compare data all together

What's Next ? New quantification effort

(Anderson et al., #2273 this meeting)

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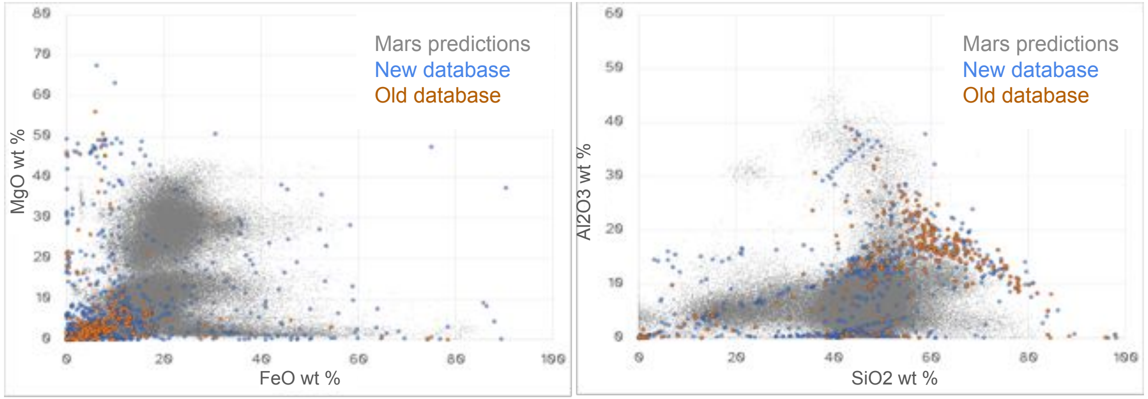
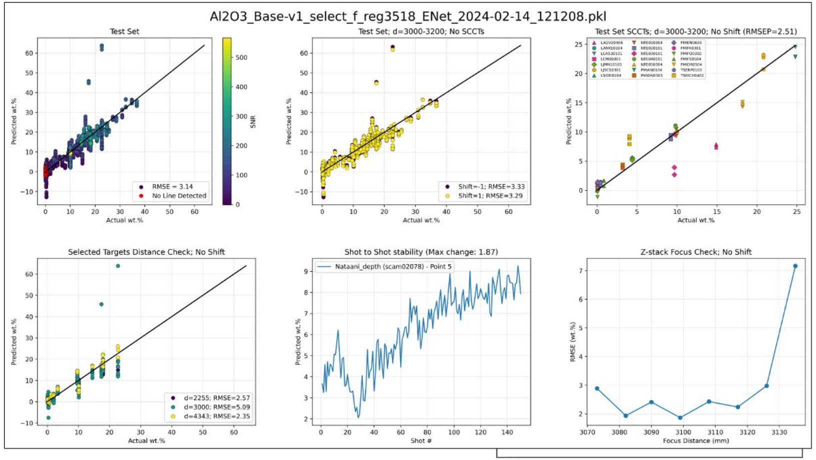
- New database has been acquired
  - Wider range of compositions to better match Mars observations
  - Over twice the number of targets (793 targets)
  - Varying distances, z-stacks



- New pipeline effort
  - Enabling to optimise the pre-processing steps
  - Improving consistency between models
  - Enabling apples to apples comparisons between model candidates
    - RMSE from test set (including shift in wavelength)
    - RMSE on SCCTs
    - RMSE on some targets at different distances
    - Shot to shot stability
    - Z-stack focus check
  - Use of superlearners, along with blended submodels
  - Several models to compare:
    - ElasticNet, ExtraTrees, Support Vector Machines, Gaussian Process



PDS release process

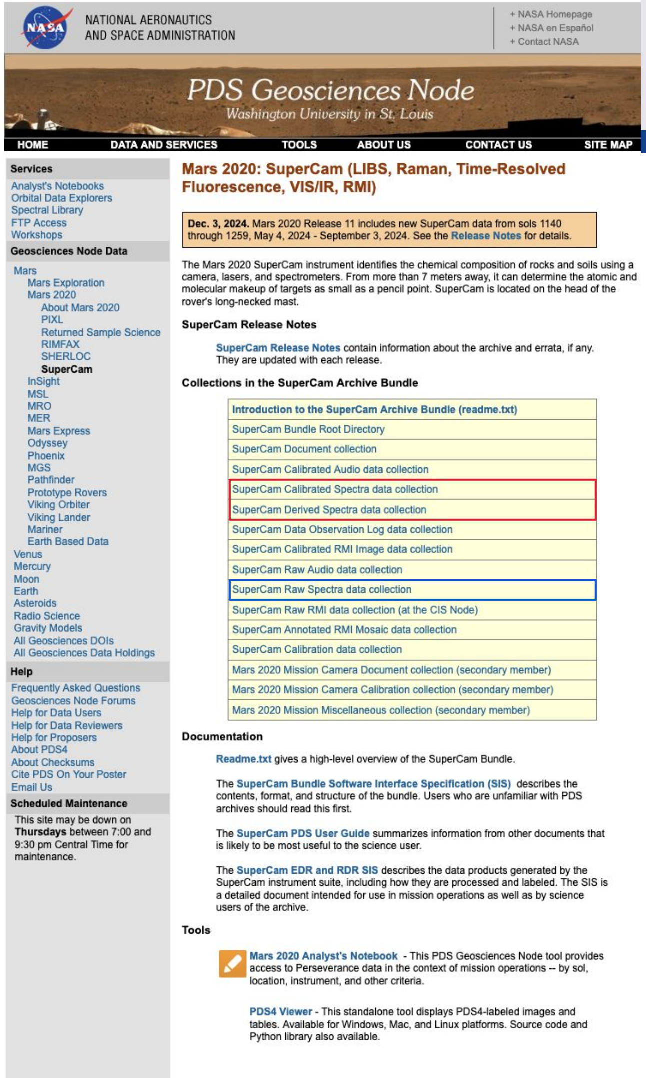
- Some quality-checks are done before delivering the data to PDS *(keep in mind that all EDR are released)*

- CDR spectra (point to point) can be removed from the release if:
  - low signal (total intensity < 1.10^{14})
  - Focus not optimum:
    - By checking the focus curves and their spacing
  - Distance > 6.5m

- MOC are removed for same filters, and when:
  - TiO2 is > 2.4 wt%
  - Sum of Oxides > 121 wt% (>3sigma)
  - Sum of oxides > 107 % (1sigma) are released but there is a note in the masterlist

- Mosaics for data out of focus (for LIBS activity only) are not delivered either

- LIBS fit files contain several data (see intro. slides for CDR structure):
  - "statistics": mean, median, and standard deviation (first 5 shots removed)
  - "spectra": all shots

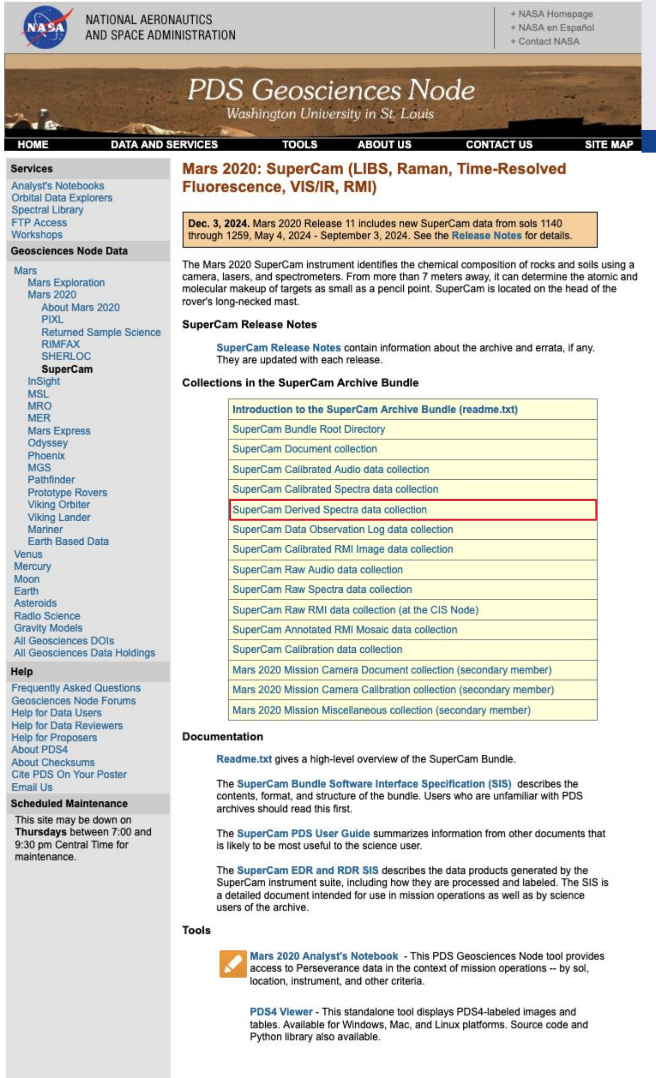


PDS release process

- MOC (compositions) can be found here:
  - https://pds-geosciences.wustl.edu/m2020/urn-nasa-pds-mars2020_supercam/data_derived_spectra/

Training set Quartiles	SiO2		TiO2		Al2O3		FeOT		MgO		CaO		Na2O		K2O
Min	0.02		0.01		0.01		0.04		0.03		0.01		0.01		0.01
1st	48.07		0.41		10.1		4.25		1.695		0.4		0.4		0.53
Med	55.03		0.685		15.41		6.185		2.93		1.76		1.75		1.9
3rd	61.75		0.9		18.1		9.3225		5.12		8.73		3.38		3.65
Max	88.38		3.39		38.79		74.96		49.18		35.67		6.72		8.88
RMSEP	6.1		0.3		1.8		3.1		1.1		1.3		0.5		0.6
Precision	1.6		0.02		0.74		0.93		0.47		0.6		0.2		0.2

cdr_fname	SiO2	SiO2_stdev	TiO2	TiO2_stdev	Al2O3	Al2O3_stdev	FeOT	FeOT_stdev	MgO	MgO_stdev	CaO	CaO_stdev	Na2O	Na2O_stdev	K2O	K2O_stdev	Total	distance_mm	Tot.Em.
scam_0012_0668002890_477_cl1_scam15210_maaz______01p	43.74	1.28	0.68	0.02	9.15	1.45	12.91	1.56	5.73	0.49	4.79	0.3	1.52	0.32	0.72	0.33	79.24	3126	7.04E+14
scam_0015_0668272463_966_cl1_scam15218_tselchee______01p	55.81	2.17	0.62	0.02	10.89	1.28	7.59	2.14	1.66	0.6	3.52	0.52	3.45	0.41	2.46	0.38	86	3192	4.09E+14
scam_0015_0668272508_963_cl1_scam15218_tselchee______02p	61.21	3.1	0.48	0.03	10.38	1.47	9.26	2.55	0.78	0.49	1.99	0.63	3.37	0.36	2	0.45	89.47	3192	5.34E+14
scam_0015_0668272553_991_cl1_scam15218_tselchee______03p	50.96	1.43	0.74	0.06	8.92	1.64	21.78	5.8	2.1	0.75	7.54	0.79	2.22	0.24	0.88	0.26	95.14	3192	8.00E+14
scam_0015_0668272816_977_cl1_scam15218_tselchee______05p	49.73	9.3	0.52	0.06	7.69	1.5	13.03	2.22	5.83	6.53	3.28	0.4	2.64	0.51	1.82	0.54	84.54	3187	6.84E+14
scam_0015_0668272861_983_cl1_scam15218_tselchee______06p	47.95	2.33	0.69	0.01	7.03	1.27	12.41	2.08	5.48	1.38	3.75	0.35	3.11	0.23	0.9	0.42	81.32	3187	6.95E+14
scam_0015_0668272906_994_cl1_scam15218_tselchee______07p	59.73	3.25	0.37	0.19	14.67	1.06	5.44	2.72	1.57	0.79	4.5	0.14	3.65	0.15	1.74	0.42	91.67	3189	4.84E+14
scam_0015_0668272951_964_cl1_scam15218_tselchee______08p	39.61	2.33	0.65	0.06	6.15	1.42	11.01	1.71	10.9	2.51	9.93	2.93	2.24	0.24	0.76	0.41	81.25	3189	9.08E+14
scam_0015_0668272996_966_cl1_scam15218_tselchee______09p	45.86	1.94	0.65	0.07	3.36	0.75	46.82	3.98	1.31	0.33	3.49	0.41	1.05	0.15	0.42	0.33	102.96	3189	1.54E+15
scam_0015_0668273137_969_cl1_scam15218_tselchee______10p	45.79	2.1	0.54	0.08	10.92	2.06	13.99	2.06	3.64	1.14	5.13	0.89	3.25	0.57	1.45	0.67	84.71	3192	5.03E+14
scam_0027_0669344001_357_cl1_scam01027_scct_pmian0106______15p	41.19	1.19	0.2	0.01	25.03	1.01	3.52	2	1.49	0.53	5.86	0.19	5.96	0.34	1.44	0.21	84.69	1556	2.66E+14
scam_0027_0669344412_399_cl1_scam02027_scct_pmian0106______15p	45.1	1.3	0.04	0	25.66	0.64	3.3	0.05	1.39	0.3	6.19	0.29	5.32	0.12	1.64	0.17	88.64	1556	2.10E+14
scam_0028_0669424371_181_cl1_scam01028_iina______01p	58.31	1.62	0.31	0.03	7.54	0.53	9.6	8.1	0.95	0.2	0.88	0.2	1.84	0.21	4.03	0.43	83.46	3177	1.23E+15
scam_0028_0669424511_056_cl1_scam01028_iina______02p	67.62	1.37	0.41	0.07	13.35	0.96	3.66	1.61	1.23	0.21	3.64	0.51	4.37	0.2	2.27	0.42	96.55	3177	6.01E+14
scam_0028_0669424650_124_cl1_scam01028_iina______03p	59.15	1.67	0.35	0.03	6.3	1.08	42.16	10.07	0.74	0.14	1.55	0.46	2.64	0.18	2.03	0.39	114.92	3177	1.45E+15
scam_0028_0669424790_046_cl1_scam01028_iina______04p	60.12	3.3	0.45	0.11	7.41	1.29	29.8	5.17	1.9	0.45	2	0.74	3.1	0.59	1.72	0.48	106.5	3180	1.43E+15
scam_0028_0669424927_993_cl1_scam01028_iina______05p	56.38	2.99	0.68	0.12	7.03	1.41	36.96	3.84	1.6	0.51	3.21	0.65	3.31	0.3	1.19	0.44	110.36	3180	1.64E+15
scam_0028_0669425240_031_cl1_scam01028_iina______06p	48.4	1.52	0.33	0.14	17.77	1.01	12.54	1.18	1.85	0.29	6.74	0.51	3.85	0.22	0.24	0.3	91.72	3172	8.65E+14
scam_0028_0669425379_071_cl1_scam01028_iina______07p	62.9	3.51	0.61	0.05	10.9	1.11	5.29	4.05	0.92	0.25	2.16	0.58	3.93	0.28	2.96	0.47	89.67	3172	1.21E+15
scam_0028_0669425518_039_cl1_scam01028_iina______08p	60.45	8.36	0.49	0.13	5.3	1.21	13.49	2.38	2.13	0.77	3.03	0.57	1.92	0.33	1.59	0.42	88.4	3174	1.27E+15
scam_0028_0669425657_056_cl1_scam01028_iina______09p	53.73	2.85	0.34	0.16	15.3	1.15	11.99	1.73	1.56	0.37	4.18	0.24	4.4	0.27	1.61	0.39	93.11	3174	7.87E+14
scam_0028_0669425885_040_cl1_scam01028_iina______10p	55.42	1.83	0.59	0.05	20.67	1.54	6.36	1.02	1.74	0.22	4.73	0.16	4.78	0.22	1	0.28	95.29	3171	9.74E+14
scam_0034_0669954315_530_cl1_scam01034_scct_pmifs0505______10p	40.51	2.22	0.02	0.01	2.67	0.72	40.62	1.56	4.49	1.01	4.2	0.07	0.58	0.12	0	0	93.09	1560	4.95E+14
scam_0034_0669954755_560_cl1_scam02034_scct_tsrich0404______07p	31.38	5	1.45	0.24	7.46	0.96	5.16	2.88	2.6	0.23	4.56	0.34	1.57	0.07	34.87	2.01	89.05	1559	2.55E+14



List of papers and links to useful LIBS tools

Instrument and calibration targets:

- Wiens et al., 2021 (Body Unit); https://doi.org/10.1007/s11214-020-00777-5
- Maurice et al., 2021 (Mast Unit); https://doi.org/10.1007/s11214-021-00807-w
- Manrique et al., 2020 (Calibration targets, design); https://doi.org/10.1007/s11214-020-00764-w
- Madariaga et al., 2021 (Calibration targets, homogeneity); https://doi.org/10.1016/j.aca.2022.339837
- Cousin et al., 2021 (Calibration targets, characterization); https://doi.org/10.1016/j.sab.2021.106341.
- Legett et al. 2022 (Instrument response function); https://doi.org/10.1364/AO.447680

SuperCam LIBS papers:

- Anderson et al., 2022 (MOC): https://doi.org/10.1016/j.sab.2021.106347
- Manelski et al., 2024 (plasma density): https://10.1016/j.sab.2024.107061
- Manelski et al., in prep (Ni quantification)
- Gabriel et al., in prep (Minors quantification)
- Wolf et al., in prep (Cl quantification)

Team papers using LIBS data:

- Wiens et al., 2022 (crater floor, perchlorate detection); https://doi.org/10.1126/sciadv.abo3399
- Clavé et al., 2023 (crater floor, carbonate detection); https://doi.org/10.1029/2022JE007463
- Beyssac et al., 2023 (Seitah, olivine detection); https://doi.org/10.1029/2022JE007638
- Udry et al., 2022 (Màaz, lava flows): https://doi.org/10.1029/2022JE007440
- Beck et al., accepted (silica and quartz, hydrothermalism)
- Hausrath et al., 2022 & 2024 (regolith): https://doi.org/10.1029/2023JE008046 & https://doi.org/10.1029/2022JE007433
- Cousin et al., 2024 (regolith diversity): https://doi.org/10.1016/j.icarus.2024.116299

RSS papers (samples)

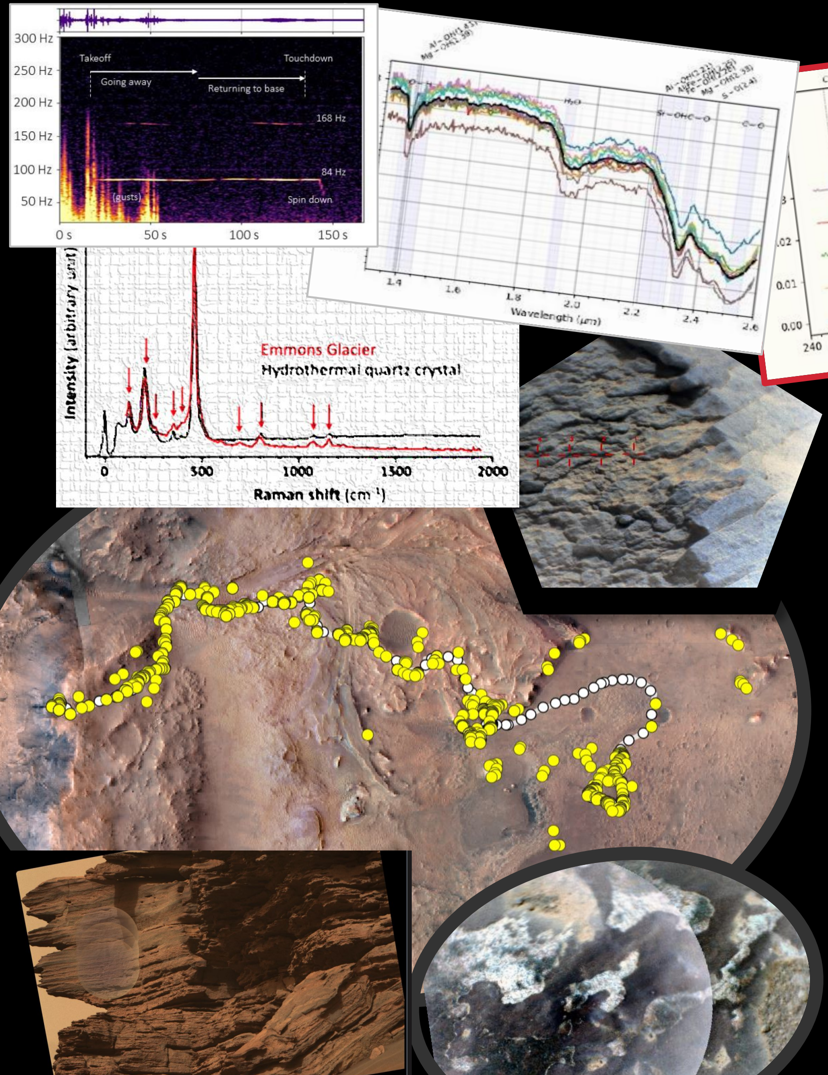
- Simon et al., 2023 (Crater floor samples); https://doi.org/10.1029/2022JE007474
- Bosak et al., 2024 (Fan Front samples); https://doi.org/10.1029/2024AV001241

Useful links:

- NIST dedicated to LIBS: https://physics.nist.gov/PhysRefData/ASD/LIBS/libs-form.html
- NIST Atomic Spectra lines database: https://physics.nist.gov/PhysRefData/ASD/lines_form.html
- CQUEST:
  - Presentation: https://pds-geosciences.wustl.edu/workshops/chemcam-workshop-2014/4._CQUEST_Mars_LIBS_Emission_Line_Tool_Cousin.pdf
  - Tool:
- Ternary Diagram tool:
  - Poster #2033, Essunfeld Ari.
- Python Hyperspectral Analysis Tool (PyHAT)
  - https://code.usgs.gov/astrogeology/pyhat

Don't hesitate to reach out to SuperCam team members if you have any questions or need help with LIBS data !

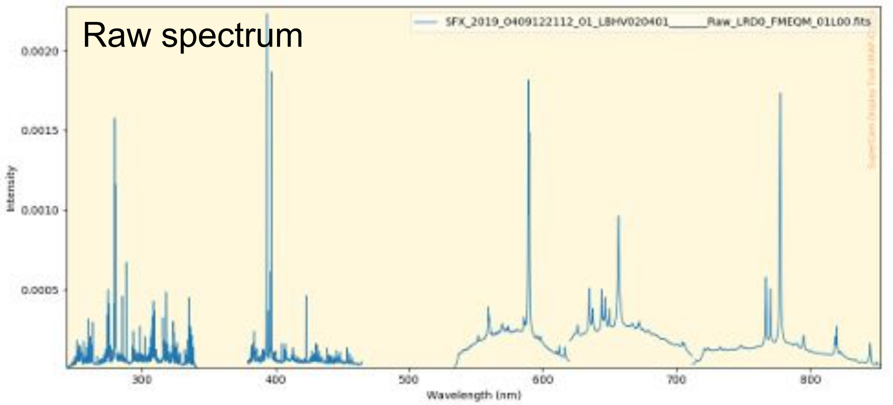

Thank
You

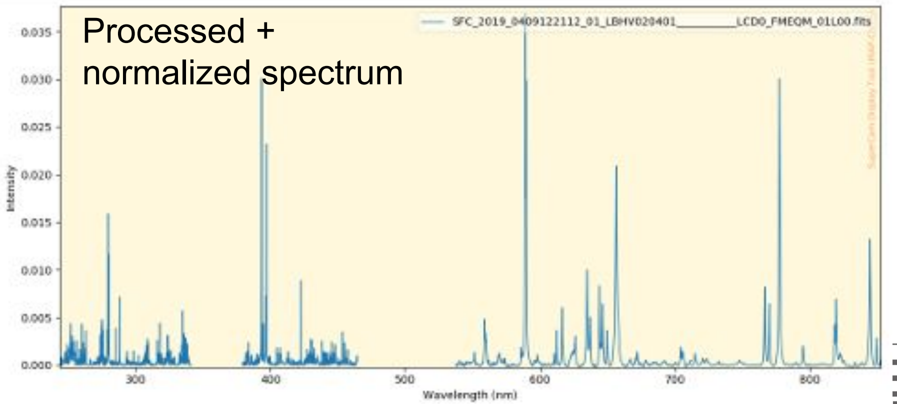


Backup Slides

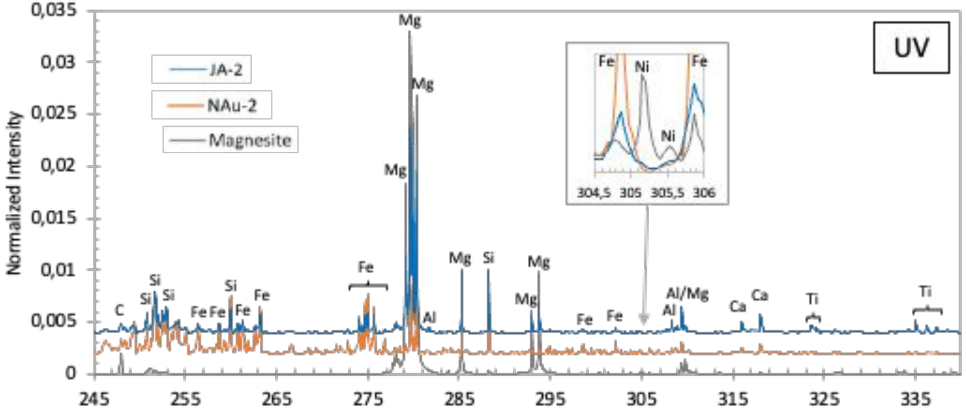
LIBS Data Processing

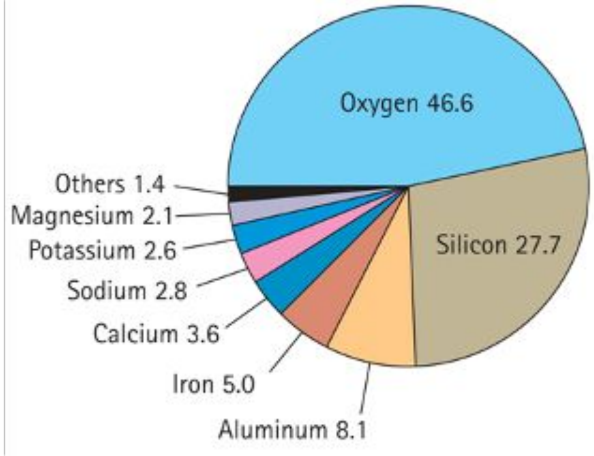
- Remove spikes (cosmic rays)
- Subtract "dark" spectra (collected when there is no LIBS pulse, to correct for thermal noise)
- Denoise spectra
- Convert to photons using instrument response
- Stitch the Green, Orange and Red ranges together
- Wavelength calibration
- Subtract continuum
- Convert to radiance





LIBS Quantification





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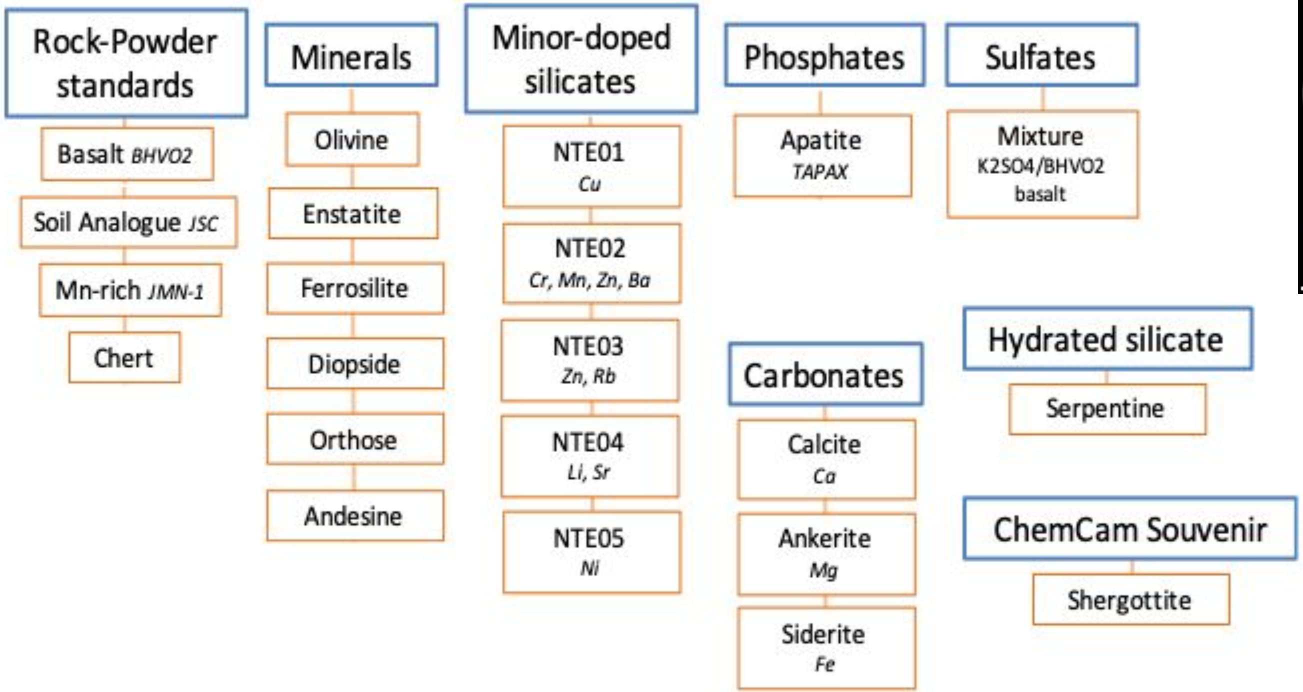
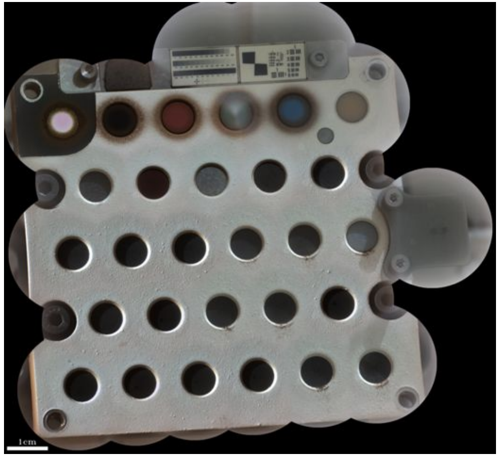
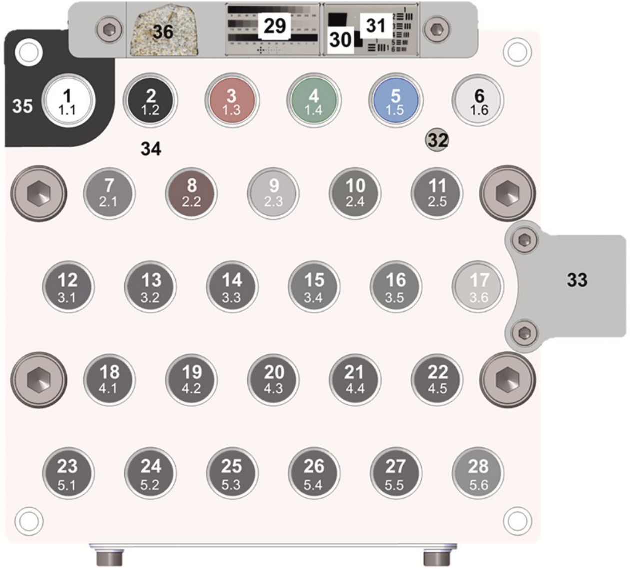
SuperCam calibration targets - LIBS dedicated

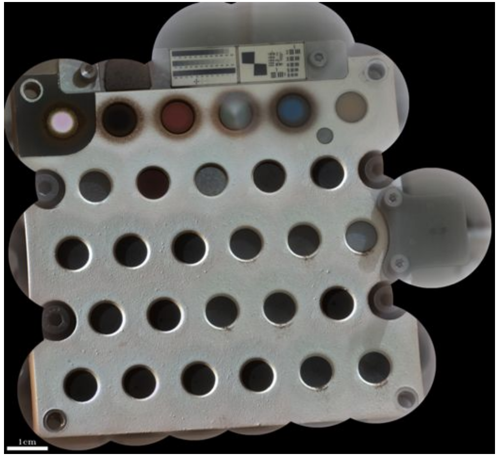




SuperCam calibration targets - LIBS dedicated



Position	Target #	TargetName	Description	Science Intent
2.1	7	TSRICH0404	BHVO-2 basalt and K sulfate mixture	Sulfur detection
2.2	8	LCMB0006	Chert	Past acqueous environment and astrobiology interest
2.3	9	LCA530106	Calcite	Carbonate calibration
2.4	10	PMIFS0505	Ferrosilite	Stoichiometric reference
2.5	11	TAPAG0206	Fluoro-Chloro-Hydro Apatite	Volatile detection, phosphate
3.1	12	PMIOR0507	Orthoclase	Stoichiometric reference
3.2	13	PMIDN0302	Diopside	Stoichiometric reference
3.3	14	PMIFA0306	Olivine	Stoichiometric reference
3.4	15	PMIAN0106	Andesine	Stoichiometric reference
3.5	16	PMIEN0602	Enstatite	Stoichiometric reference
3.6	17	TSERP0102	Serpentine/Talc	Hydrated silicate, alteration product
4.1	18	LBHVO20406	BHVO-2 standard basalt	Mars analog, basaltic composition
4.2	19	LJSC10304	JSC-1 standard	Mars soil analog
4.3	20	LANKE0101	Ankerite	Carbonate calibration
4.4	21	LSIDE0101	Siderite	Carbonate calibration
4.5	22	LJMN10106	JMN-1 standard Mn nodule	Mn enrichment, coating detection
5.1	23	NTE010301	Basalt dopped in minor elements	Calibration and quantification of Cu, Zn
5.2	24	NTE020106	Basalt dopped in minor elements	Calibration and quantification of Mn, Ba, Cr
5.3	25	NTE030106	Basalt dopped in minor elements	Calibration and quantification of Zn
5.4	26	NTE040106	Basalt dopped in minor elements	Calibration and quantification of Li, Sr
5.5	27	NTE050301	Basalt dopped in minor elements	Calibration and quantification of Ni
5.6	28	SHERG02	Shergottite	ChemCam cal. Target replicate, cross calibration
/	33	TITANIUM	Titanium	Wavelength calibration



Cousin et al., 2021 (Calibration targets, characterization); https://doi.org/10.1016/j.sab.2021.106341.

MARS 2020 SUPER CAM

PDS links (check introduction slides for LIBS filenames)

- Raw (EDR) files can be found here:
  - https://pds-geosciences.wustl.edu/m2020/urn-nasa-pds-mars2020_supercam/data_raw_spectra/sol_00214/
- CDR can be found here:
  - https://pds-geosciences.wustl.edu/m2020/urn-nasa-pds-mars2020_supercam/data_calibrated_spectra/
- MOC (compositions) can be found here:
  - https://pds-geosciences.wustl.edu/m2020/urn-nasa-pds-mars2020_supercam/data_derived_spectra/
- Masterlist can be found here:
  - https://pds-geosciences.wustl.edu/m2020/urn-nasa-pds-mars2020_supercam/data_observation_log/