A Preliminary Study Comparing ChemCam Data with LIBS on Martian Meteorite NWA 7034

S. R. Gordon[1], H. E. Newsom[1], C. B. Agee[1], S. M. Clegg[2], J. Lasue[3], R. C. Wiens[2], A. R. Santos[1], MSL Team, [1]Institute of Meteoritics, UNM, Albuquerque, NM (gordons@unm.edu), [2]Los Alamos National Laboratory (LANL), Los Alamos, NM, [3]Institut de Recherche en Astrophysique et Planétologie (IRAP), Toulouse, France.

Introduction

- The ChemCam (Chemistry and Camera) instrument on the Mars Science Laboratory (MSL) *Curiosity* rover uses laser-induced breakdown spectroscopy (LIBS) to remotely analyze rock and soil targets on Mars.
- LIBS Instrumentation can profile up to 1 mm of depth into a rock [1].
- Martian meteorite NWA 7034 (Figure 1) LIBS analyses done at LANL can be compared to electron microprobe analyses (EPMA) of the meteorite and to ChemCam LIBS targets to show similarities between the basaltic breccia and rocks and soils found in Gale crater on Mars.

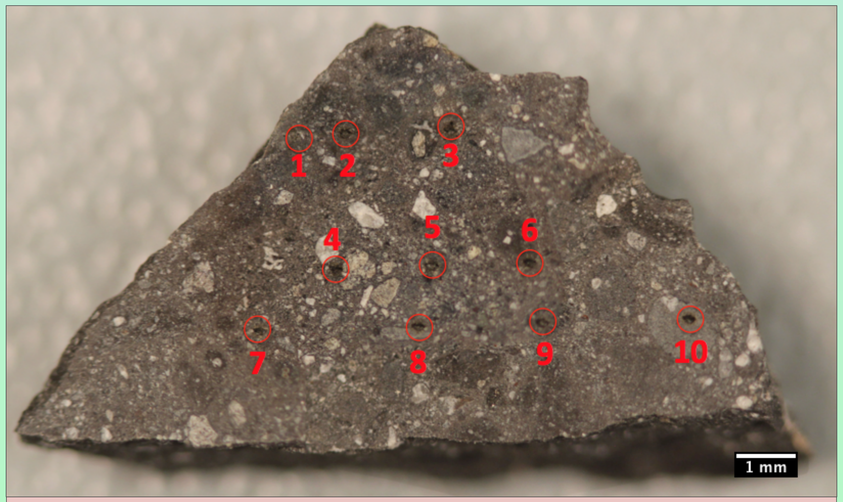

Figure 1: Sample of NWA 7034 (~12 mm across at longest edge). Locations (Location 1: 50 laser shots, Locations 2-10: 150 laser shots) are highlighted and numbered.

Methods

- NWA 7034 was placed in a chamber filled with 7 Torr CO_2 at a distance of 1.6 m.
- First shot was a test of laser pit visibility; 50 shots fired at 12 mJ per pulse at repetition rate of 3 Hz.
- Other nine locations pulsed with 150 laser shots each to ensure visibility of laser pits; normal ChemCam target has 30 shots per location.
- LIBS spectra from ChemCam and NWA 7034 were analyzed using Partial Least Squares (PLS) from a calibration set analyzed with LIBS at Los Alamos National Laboratory (LANL) [1].
- NWA 7034 analyzed with an updated PLS calibration set which includes 482 test samples of various petrologic types [2].
- Analyses give major oxide concentrations for SiO_2, TiO_2, Al_2O_3, FeO, MgO, CaO, Na_2O, and K_2O, as well as some minor elements [1], but only major oxides were evaluated in this study.
- After the LIBS experiment, EPMA was used to analyzed the clasts containing LIBS Locations 9 and 10.

LIBS Location	SiO_2	TiO_2	Al_2O_3	FeOT	MgO	CaO	Na_2O	K_2O	Total
1	49.0	1.51	9.40	14.6	10.2	5.20	3.00	0.60	**93.5**
2	44.8	1.47	9.40	12.7	8.40	8.60	2.70	0.00	**88.1**
3	49.7	1.26	9.30	13.1	13.5	4.60	2.70	0.10	**94.3**
4	48.5	1.47	10.00	14.7	11.5	4.90	2.80	0.40	**94.3**
5	48.8	1.34	9.40	13.8	10.8	5.70	2.80	0.60	**93.2**
6	43.4	1.56	8.50	14.2	7.50	10.3	2.60	0.10	**88.2**
7	51.6	0.99	9.00	12.8	12.9	4.50	2.80	0.40	**95.0**
8	48.1	1.26	9.60	14.6	9.40	5.60	2.90	0.10	**91.6**
9	47.5	1.28	8.80	14.0	11.5	6.00	2.70	0.10	**91.9**
10	52.1	0.62	8.70	12.2	12.7	4.30	2.80	0.00	**93.4**
Average	48.4	1.28	9.21	13.7	10.8	5.97	2.78	0.24	92.3

Table 1: PLS-1 results for NWA 7034 using the calibration set describe in [2]. All values are percentages.

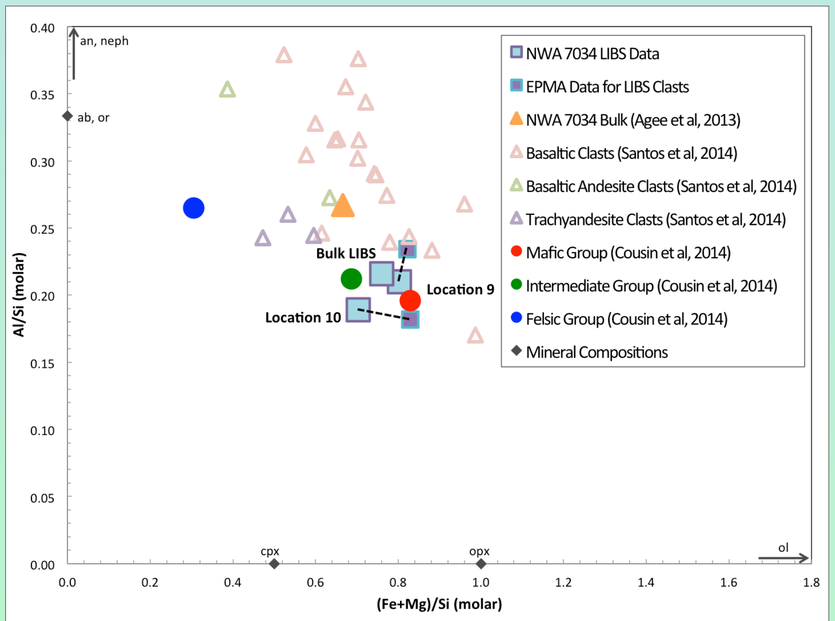

Figure 2: Elemental comparison plot of Al/Si vs. (Fe+Mg)/Si of LIBS clast data for NWA 7034 (purple and teal squares – Location 9 clast, Location 10 clast LIBS and EMPA connected with dotted lines), LIBS bulk data for NWA 7034 (orange triangle), EPMA for NWA 7034 (red, green, and purple triangles – bulk, basaltic clasts, basaltic andesite clasts, and trachyandesite clasts), and the three types specified in [6] (circles – mafic, intermediate, and felsic). EPMA data of LIBS locations 9 and 10 are similar to the LIBS data within the LIBS RMSEP (Root Mean Standard Error of Prediction). Mineral end members albite (ab), orthoclase (or), anorthite (an), nepheline (neph), orthopyroxene (opx), clinopyroxene (cpx) and olivine (ol) are also plotted for comparison.

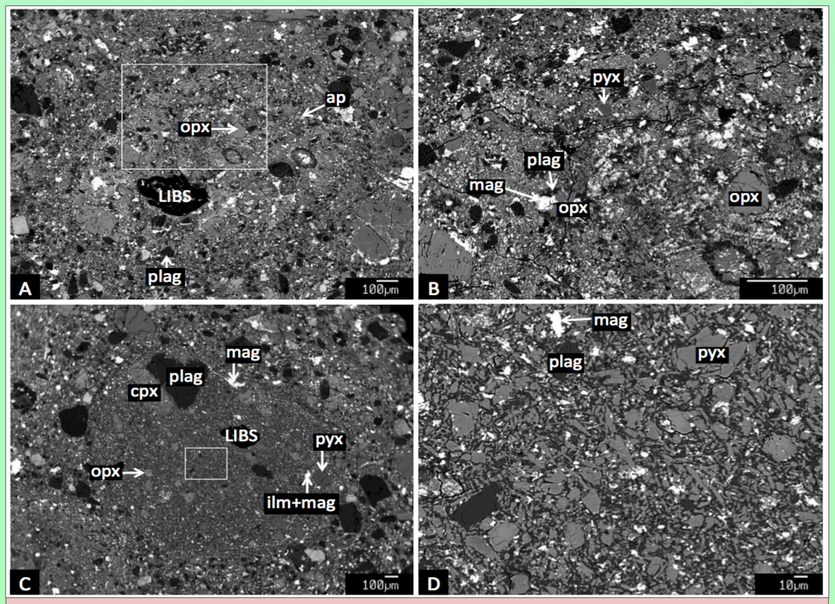

Figure 3: Backscattered Electron (BSE) images of clasts that include LIBS Locations 9 (A ,B) and 10 (C,D). Insets shown in A and C are magnified in B and D, respectively. Label definitions: LIBS = LIBS pit, opx = low-Ca pyroxene, cpx = high-Ca pyroxene, pyx = pyroxene, plag = plagioclase, ap = Cl-rich apatite, ilm = ilmenite, mag = Cr-rich magnetite.

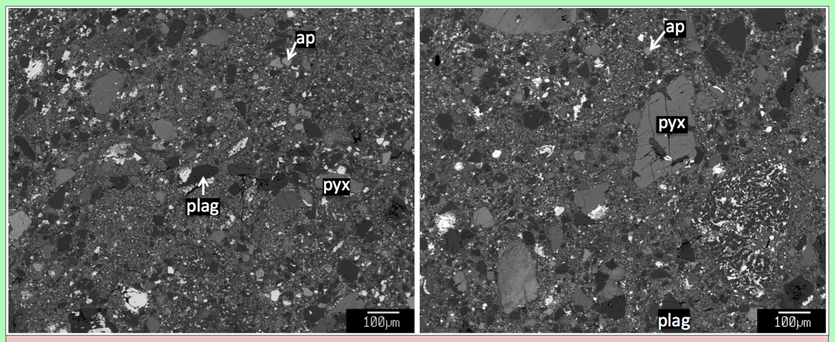

Figure 4: Backscattered Electron (BSE) images of standard matrix in NWA 7034 for comparison with BSE images of clasts in Figure 3. Most LIBS locations are on the matrix as opposed to clasts. Label definitions are the same as in the previous figure.

NWA 7034 PLS Results

- First use of updated calibration set for LIBS PLS [2].
- All 10 locations show similar basaltic composition (Table 1) due to the small-scale (smaller than the ~350 µm LIBS shot) heterogeneity of NWA 7034.
- Anti-correlation between CaO and total reported oxides suggests CaO is linked to a major element not reported by PLS data and not readily available with LIBS (may be a sulfate, $CaCl_2$, or Cl-rich apatite).
- CIPW norm of bulk average LIBS composition: 37% feldspar, 41% pigeonite, 12% olivine.
- CIPW norm of microprobe analyses reported in [3]: 45% feldspar, 27% pigeonite, 19% olivine.
- Results for CIPW of LIBS and EPMA data are similar, taking into account the limited number of LIBS observations on the coarse-grained matrix.
- Totals below 100% are normal for LIBS major oxide analyses; there is up to a 10% contribution from elements in the amorphous component that are not easily detected by LIBS instrumentation [4].

Comparison with Microprobe and ChemCam Data

- Comparison focuses on NWA 7034's Locations 9 and 10, which hit clasts in the meteorite (see Figure 1).
- EPMA analyses cover a spot ~40 microns across, while LIBS shots cover ~350 microns. Thus, results are not expected to be completely identical as each instrument focuses on a different scale in the meteorite clasts (see Figure 3).
- Figure 2 shows an elemental ratio comparison plot of Al/Si versus (Fe +Mg)/Si for NWA 7034 LIBS locations, igneous clasts within NWA 7034 analyzed by electron probe microanalysis (described in [5]) and the felsic, intermediate and mafic categories of ChemCam targets suggested in [6].
- Microprobe and LIBS bulk and clast data plot within error of the mafic and intermediate groups defined by [6].
- EPMA of the clasts shot with LIBS Locations 9 and 10 are closest to the LIBS clast data than EPMA of other clasts in the meteorite.
- LIBS clasts plot within error of the microprobe basaltic clast range, although they fall in the low Al/Si range, suggesting the LIBS clasts can be classified as basaltic.
- LIBS and EPMA of the same clasts in the sample (LIBS locations 9 and 10) show similar results (see Figure 2) within the RMSEP of the LIBS instrumentation.

Conclusions and Future Work

- Comparison of LIBS and microprobe data of clasts in NWA 7034 allows better interpretation of both LIBS and EPMA results for NWA 7034 and of LIBS results for ChemCam targets.
- Using the same PLS techniques proven effective for ChemCam data, we begin to see similarities between the meteorite and mission data in composition and petrologic types.
- LIBS and EPMA results agree within error, supporting ChemCam's reliability in predicting oxide compositions on a fine (~350 micron) scale.
- Continuing work will compare LIBS and EPMA of more clasts in the meteorite sample. Comparison with ChemCam rock and soil targets may lead to the creation of a classification scheme that takes into account both sets of data.

References

[1] Wiens R. C. et al. (2012) *Space Sci Rev, 170,* 167-227. [2] Clegg S. et al. (2014) *LPSC,* #2378. [3] Agee C. B. et al. (2013) *Science, 339,* 780-785. [4] Leshin, L. et al. (2013) *Science, 341,* DOI: 10.1126/science.1238937. [5] Santos R. et al. (2014) This Meeting. [6] Cousin A. et al. (2014) *Icarus,* in press.

Acknowledgements

Many thanks to Rhonda McInroy and Nina Lanza for their help in experimental setup at LANL, and Mike Spilde and Alison Santos for their help using EPMA. This project was funded by the New Mexico Space Grant Consortium's Graduate Research Fellowship and MSL ChemCam.