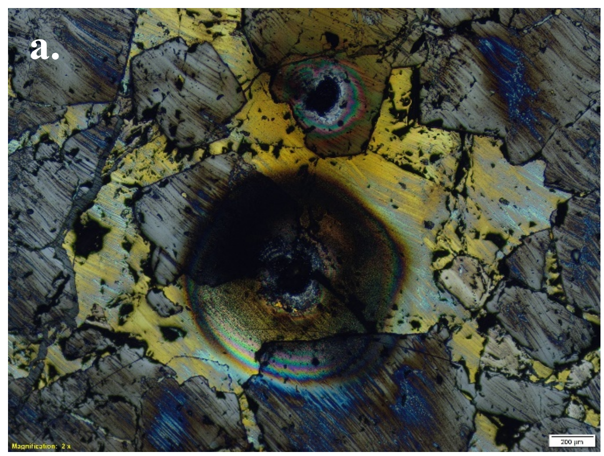
LIBS Shock Wave Deformation Area: Material redistribution and mineral recrystalization. P. Such[1], E. Lalla[1], C. Gilmour[1], M. Daly[1]. 1-Center for Research in Earth and Space Science. Petrie Science and Engineering Building. York University - Toronto, Canada. Corresponding author: suchpam@yorku.ca

Introduction: The Shock Wave Deformation Area (SWDA) created from Laser-Induced Breakdown Spectroscopy (LIBS) was examined on multiple samples with an Atomic Force Microscope (AFM) and Scanning Electron Microscope equipped with an Energy Dispersive X-Ray Spectrometer (SEM-EDX). Terrestrial samples with compositions similar to those of Mars and ureilite meteorites were analyzed in this study. Redistribution and redeposition of material around the SWDA was observed with alteration halos and compositional changes due to shock-induced mineral recrystallization. Micro Raman spectroscopy was also collected before and after LIBS to acquire spectral data for comparison. The use of AFM, SEM-EDX, and micro Raman spectroscopy to study compositional modifications caused by LIBS has never been conducted prior to this investigation. Accordingly, observations of these modifications have implications for the future development and improvement of combined LIBS and Raman instruments for space explorations missions, such as the LIBS-Raman spectrometer on the ESA ExoMars mission [1] and the SuperCam on NASA's Mars 2020 rover [2].

Study: Samples of bytownite sub-volcanic lava domes with silica-calcite-metal (sulfides, oxides) veins were selected to represent the compositions of Martian volcanic rocks and ureilite meteorites. An optical microscopic assessment was first completed on each sample to classify the mineralogy and petrology of the terrestrial analogs. Prior to LIBS, SEM-EDX was performed to obtain the chemical composition of the samples. Based on this compositional analysis, we chose specific areas in the samples to target with LIBS. During AFM analysis, alteration halos were observed around the LIBS ablation holes. This phenomena represents the SWDA (Fig. 1). AFM topography maps (Fig. 2) show the redistribution and redeposition of material around the ablation holes up to 2 microns in the immediate area and up to 1 micron in the surrounding areas adjacent to the holes. SEM-EDX analysis after LIBS revealed compositional changes among the redistributed material due to recrystallization. In the case of the silica-calcite-metal veins (considered as ureilite meteorite analogs), the metal component of the veins (sulfides, oxides) were altered to Cu oxides accompanied by anomalous concentrations of REE and Hg up to 20% (Fig 3). For the bytownite lavas, the samples display recrystallization of plagioclase, chlorite, and olivine to a silica-rich glass in the immediate areas and anomalous concentrations of Mg, Al, and REE were found in the surrounding areas (Fig. 4). Micro Raman spectroscopy completed on the alteration halos after LIBS shows similar composition changes as those obtained with SEM-EDX. This proves that LIBS is capable of altering the mineralogy of samples. This is a caveat that deserves acknowledgement when conducting LIBS analysis.

References: [1] Ahlers B. et al. (2015) *7th Int. Conf. on Space Optics*, CNES, Toulouse, France. [2] Maurice S. et al. (2015) *EPSC Meeting,* abstract Vol. 10, EPSC2015-185.



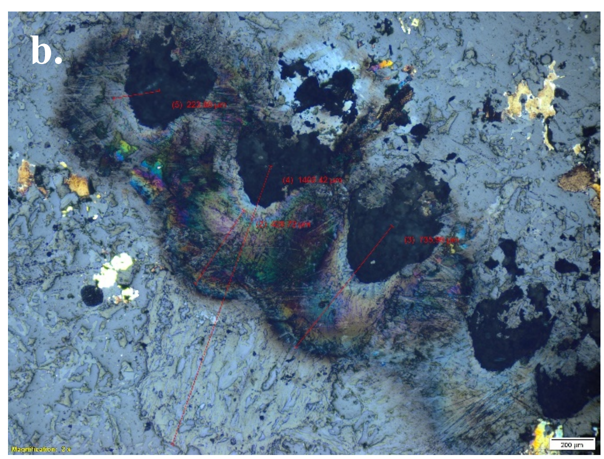


Fig. 1a. LIBS alteration halo in a ureilite meteorite analog sample. **1b.** Ablation holes in a Bytownite lava sample (Mars analog) with measured distances of the redistributed material around the SWDA.

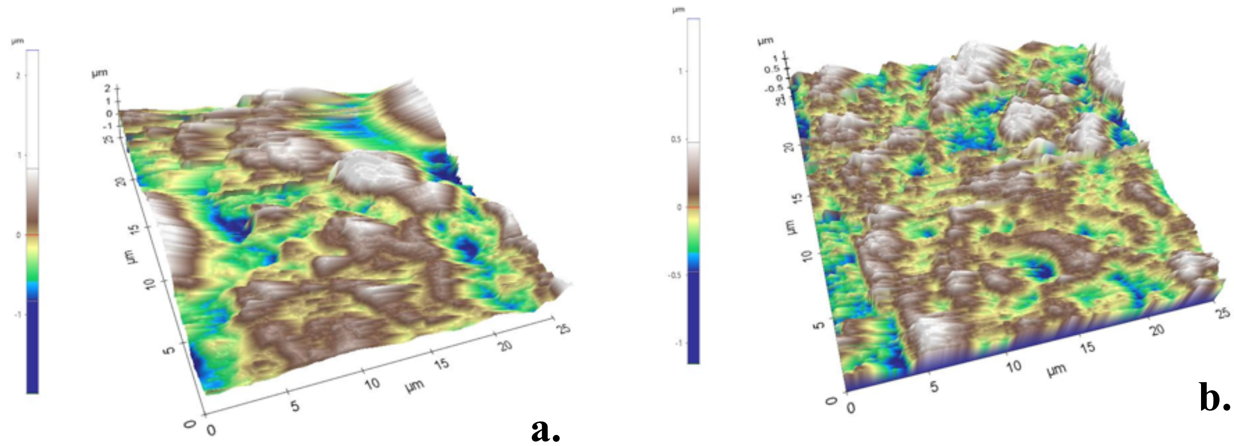
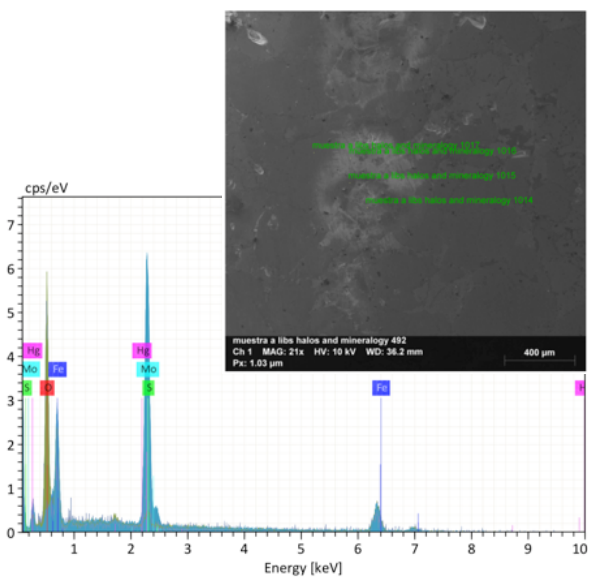


Fig. 2. AFM topography maps of the redistribution and redeposition of material. **a.** Immediate area around the LIBS ablation hole. **b.** Material surrounding the adjacent area around the ablation hole.



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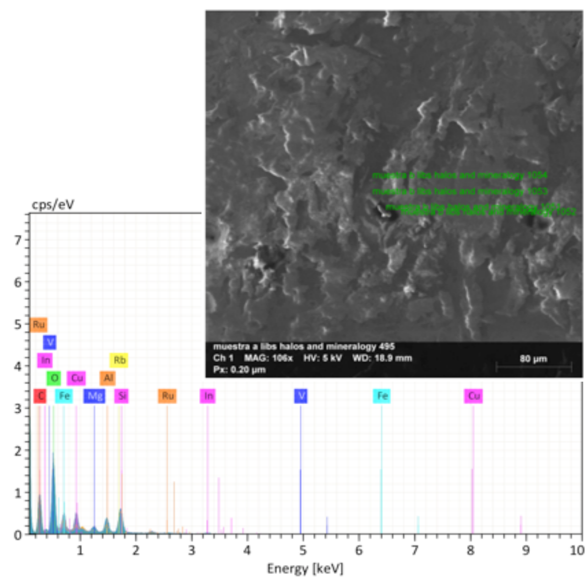
Element	At. No.	Line s.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]
Oxygen	8	K-Serie	926	5.06	3.77	13.35
Sulfur	16	K-Serie	7981	18.19	13.56	23.95
Iron	26	K-Serie	1489	58.44	43.56	44.18
Molybdenum	42	L-Serie	8484	32.56	24.27	14.33
Mercury	80	M-Serie	4666	19.91	14.84	4.19
			Sum	134.15	100.00	100.00

Fig. 3. SEM-EDX analysis of a silicate-calcite-metal vein representing ureilitic compositions. The SWDA contains concentrations of mercury up to 20%.



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Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)
Carbon	6	6735	19.43	12.86	26.79	2.91
Oxygen	8	12203	40.04	26.51	41.45	5.48
Magnesium	12	920	1.63	1.08	1.11	0.14
Aluminium	13	3440	7.01	4.64	4.30	0.40
Silicon	14	3719	16.15	10.69	9.53	0.87
Vanadium	23	2419	25.76	17.05	8.38	4.70
Iron	26	800	7.35	4.86	2.18	1.80
Copper	29	890	6.14	4.06	1.60	1.46
Rubidium	37	2804	13.04	8.63	2.53	0.73
Ruthenium	44	198	1.99	1.32	0.33	0.24
Indium	49	327	12.53	8.30	1.81	1.43
		Sum	151.06	100.00	100.00	

Fig. 4. SEM-EDX analysis of a bytownite lava sample (Mars analog). Results show an anomalous concentration of REE and magnesium in the SWDA.