Preparation and Characterization of LIRS Rock Powder Standards

I. De Souza,[1] E. Lalla[1], M. G. Daly[1,2], [1]Centre for Research in Earth and Space Science, York University, Petrie Science Building, 4700 Keele St, Toronto, M3J 1P3, Ontario, Canada. [2] (dalym@yorku.ca).

Introduction: Existing LIBS Spectral Libraries efforts for ChemCam and SuperCam now cover thousands of readings added by ChemCam from the surface of Mars alone[1]. Due to design constraints the de facto method for LIBS in space is PLS and it requires the use of homogenous calibration standards[2]. Other methods were studied extensively for ChemCam however, hardware constraints excluded them[2]. Now the use of standards plays an important part of calibration methods for LIBS and Raman. By mixing minerals analog rocks can be used to study the material impulse response to the laser. The preparation and characterization of standards for LIRS[1] is reviewed in this work.

Standard Preparation: Current preparation processes include pressing rock powders, then into glasses, or ceramics because of a homogeneity requirement by the calibration method at a beam scale of such that the certified composition of the rock powder corresponded to that observed by LIBS[2]. Another process for preparing samples for is to crush then flash sinter rock samples which consists of making a pellet from a powder using a combination of high pressure, temperature and electrical current[3].

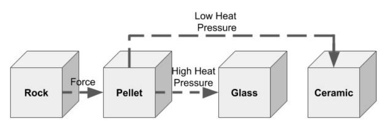
Figure 1: Quartz-Olivine pellet preparation process

A pressed powder standard was prepared using olivine and quartz rock powders for this work. Using a precision scale the weight of an empty vial was measured. Next Quartz powder was added and the sample was weighed again. Next Olivine powder was added and again the weight was measured. The ratio of Olivine to Quartz was determined to be $2.0523 \pm 0.0006:1$. Next the sample underwent mixing on a vibration table for 60 minutes. A portion of the mixed sample was then poured into the pellet press. Once loaded the pellet was pressed with 9 tons for a 10 minutes.

The pellet was then transferred to a SEM compatible mounting fixture with a bonding agent. Finally to prevent sample erosion along its perimeter an epoxy coating was applied and allowed to dry. The process can be seen in figure 1. Once dry it was taken for SEM analysis (Figure 2).

Figure 2: Standard assembly mounted in scanning electron microscope stage.

Standard Characterization: From a geological perspective there are four rock types: Igneous, Sedimentary, Metamorphic, and its source Magma.



	Powder	Pressed	Glass	Flash Sinter
Sample Code	JB2	JB2	JB2	JB2
Geologic Name	Basalt	Sandstone	Obsidian	Quartzite
Rock Type	Igneous	Sedimentary	Igneous	Metamorphic

Figure 3: Geologic Classification of JB2 through preparation processes.

For example JB-2 is a Basalt from Japan. Following figure 3 it can be seen that a Basalt (Igneous) becomes Sandstone (Sedimentary) through the crushing and pressing process and then becomes Quartzite (Metamorphic) through the applied heat and pressure from the making of glass or ceramic standards or Obsidian (Igneous) from the flash sintering process. The geologic name for the Olivine-Quartz standard prepared in this work is therefore Sandstone.

An assay of the elemental composition and mineral composition using EDX was performed. The results are presented here for the prepared standard. The elemental composition can then be used as a reference to the observed LIBS spectra for calibration. Olivine is a Forsterite-Fayalite mixture. A certified standard with $Fo_{95}Fa_5$ was selected. The Forsterite-Fayalite ratio of the Olivine used was determined to be $Fo_{95}Fa_5$ with EDX.

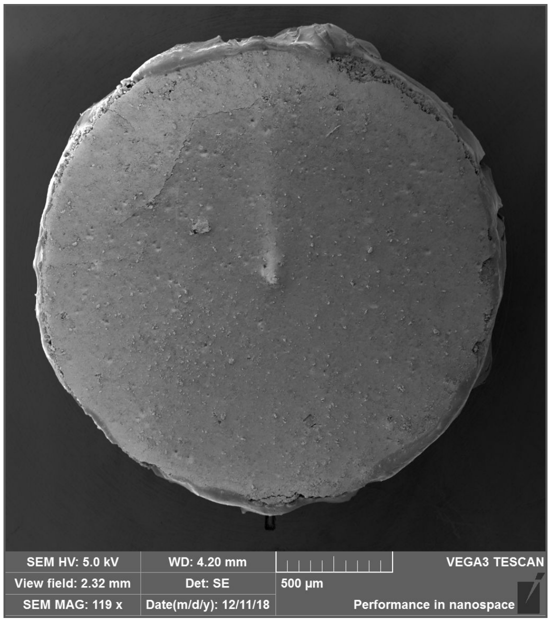


Figure 4: Wide Field image of Olivine-Quartz Standard.

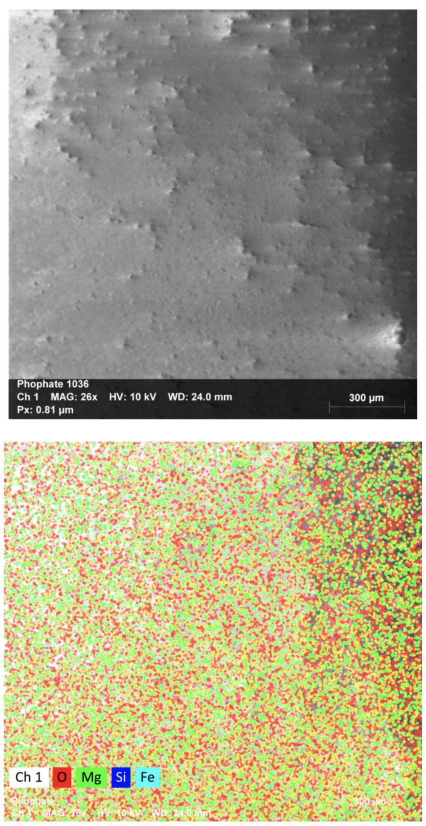


Figure 5: Olivine-Quartz Sandstone Standard SEM at Beam scale(top), and EDX Map (bottom).

Using the mass ratio of Olivine to Quartz determined during preparation the expected normalized mass of oxygen was calculated to be 44.39% This agrees well with the EDX measurement of 44.37% of the Olivine-Quartz standard. The measured EDX concentration of Silicon was higher than expected and of Magnesium lower than expected. This is due to the relative similar masses of the respective elements. A comparison of expected and measured values are shown in Table 1.

Map

Element	At. No.	Line s.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)
Oxygen	8	K-Serie	22966	46.60	44.37	57.62	5.91
Silicon	14	K-Serie	30485	38.30	36.47	26.98	1.61
Magnesium	12	K-Serie	19807	17.99	17.14	14.65	0.96
Iron	26	K-Serie	128	2.12	2.02	0.75	0.27
			Sum	**105.01**	**100.00**	**100.00**	

Figure 6: EDX elemental results of Olivine standard.

Table 1: Composition of Forsterite-Quartz Standard

Element	Expected Mass %	Measured Mass %
O	44.39	44.37
Si	20.74	36.47
Mg	31.60	17.14
Fe	3.27	2.02

Conclusions: The preparation of a homogenized pressed rock powder standard, classification, and characterization was performed. An analysis of the preparation methods and application of geological naming rules lead to producing the Olivine-Quartz Sandstone standard for LIRS. Sample elemental characterization by EDX and SEM confirmed surface homogeneity and expected elemental composition. The process shown here is found to be accurate, reproducible, and reliable.

References: [1] Cote, K. (2018) *Study of micro-laser-induced breakdown spectroscopy (µLIBS) for applications in planetary exploration.,* 7-8. [2] Wiens, et al. (2013) *Spectrochimica Acta Part B 82,* 1-27. [3] Cousin, et al. (2017) *Development of Onboard Calibration Targets for the Mars2020/SuperCam Remote Sensing Suite. LPS XXLVIII,* Abstract #2082.