

Project ESPRESSO: Exploration Roles of Handheld LIBS for Field Geology on Earth and Planetary Surfaces at the Palisades Sill. M. H. Yant¹, K.W. Lewis¹, A.H. Parker², S.M. Hörst¹, and the Project ESPRESSO Team. ¹Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, MD 21218. ²Space Sciences Division, Southwest Research Institute, Boulder, CO 80302. (marcella.yant@jhu.edu).

Introduction: A major objective of the SSERVI Project ESPRESSO (Project for Exploration Science Pathfinder Research for Enhancing Solar System Observations) investigation is to assess the role and performance of handheld Laser Induced Breakdown Spectroscopy (hLIBS) devices in the context of human space exploration while targeting specific questions of geologic interest at field analog sites. The fast data acquisition and minimal sample preparation requirements of these devices make them extremely attractive as candidate tools for future astronauts to use for geochemical mapping, resource prospecting, sample selection, and hazard identification. Recently, handheld instruments have become commercially available that enable new applications in both a conventional laboratory setting and in the field. These applications, however, have not been extensively applied to geologic field campaigns.

In order to characterize the role, utility, and development requirements for hLIBS for planetary exploration we systematically sampled ~130m of the Palisades Sill in New Jersey (**Figure 1**). The Palisades Sill is a Triassic diabase sill along the lower stretches of the Hudson River in New York and New Jersey. The sill is composed of primarily plagioclase feldspars and clinopyroxene and intrudes into the Triassic Lockatong Formation which consists primarily of lacustrine sand and siltstones [1]. The composition is strongly dependent on vertical location within the sill.

In-situ measurements of the elemental and mineralogical differentiation across the Palisades Sill, from rapidly chilled margins to a highly differentiated, late stage residual melt

horizon were collected using hLIBS. Samples were also analyzed in the lab using both hLIBS and benchtop LIBS.

We have used the collected data to 1) evaluate the ability of these field portable instruments to resolve meaningful geochemical trends, 2) assess the relationship of chemistry to both outcrop-scale spatial variability and small-scale heterogeneity, and 3) investigate the statistical accuracy for bulk geochemical estimation.

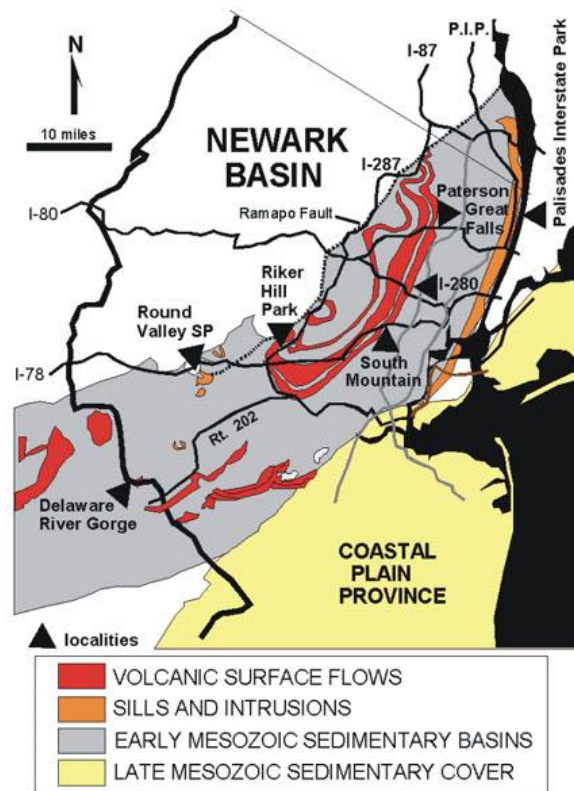


Figure 1: Map of Palisades Sill Field Area [4].

Instruments: We operated a handheld SciAps Z-300 LIBS spectrometer. This instrument offers elemental microanalysis in the field over the range of 190-950nm. It is equipped with an integrated argon purge

which allows for increased signal in the deep UV (190 – 300nm), permitting analysis of all atomic species from Hydrogen to Uranium. This instrument produces a 50 μm spot size which was used to acquire line scans. The laser spot size for rastering is 100 μm , which can be used in 4x4 – 16x16 grid pattern.

Methods: 114 samples were analyzed along the Alpine outcrop, representing approximately 110m of the sill and 20m of the underlying Lockatong formation. Line scans were acquired for 5 locations on each in-situ sample. Ten shots at each location were collected and spectra averaged. Samples were brought back to the lab and powdered to provide a homogenous sample. The powdered samples were analyzed using the same parameters and handheld instrument. The geochemical trends observed for the in-situ samples and powdered samples were compared with previous results from [2].

Results: In general, the geochemical trends observed for major oxide elements (Si, Al, Fe, Mg, Ca, Na, K, Mn, Ti, P) in the powdered samples agreed with the chemostratigraphy of the sill as previously determined in the laboratory [2]. These trends were not easily observable in the in-situ data. However, the change from basaltic sill to underlying sandstone was evident in the in-situ data. We expect that the chemical differences between the in-situ and powdered data are due to heterogeneity in the in-situ samples where grain size may exceed the hLIBS spot size.

In order to provide a better understanding of this phenomena we investigated the point-to-point variability in the hLIBS data as related to grain size in rocks using the Gini Index (G) [3]. The Gini Index is a measure of statistical dispersion that is commonly used to represent income distribution. The Gini index varies from 0 to 1, where $G=0$ expresses complete equality or uniformity and $G=1$ complete inequality.

A 16x16 raster (256 locations) was acquired for a relatively fine-, medium-, and coarse-grained sample from our suite. The fine-grained is a sandstone and the medium- and coarse-grained are basalt. For this data set, the total range of each major element oxide composition was normalized from 0-1. The Gini Index was then calculated for each oxide and the individual indices were also average into a mean Gini Index (**Table 1**).

Rocks with grains smaller than the laser spot size produce bulk rock compositions at each LIBS point and low point-to-point chemical variability, resulting in a lower G value. In contrast, analyses of rocks with grains about the size of the spot or larger contain contributions from individual grains at each point and have high point-to-point chemical variability, resulting in a higher G value.

Table 1: Gini Index (G) for major oxides and mean Gini Index.

	Fine	Medium	Coarse
G Na₂O	0.343	0.299	0.397
G MgO	0.098	0.199	0.315
G Al₂O₃	0.130	0.171	0.479
G SiO₂	0.309	0.328	0.350
G K₂O	0.084	0.131	0.202
G CaO	0.241	0.189	0.283
G TiO₂	0.321	0.338	0.463
G FeO	0.180	0.211	0.247
G Mean	0.213	0.233	0.342

References: [1] Walker, K. R., (1969) Geological Society of America Memoir, v. 115, p. 175 – 187. [2] Goring, M. L., and Naslund, H. R., (1995), Contrib. Mineral. Petrol. 119:263–276. [3] Rivera-Hernández, F. *et al.*, (2019), Icarus, 321, 82–98. [4] <http://geologycafe.com/nyc/mesozoic/newarkbasin.htm>