**VOLUME MEASUREMENTS OF LASER-GENERATED PITS FOR IN SITU GEOCHRONOLOGY USING KArLE (POTASSIUM-ARGON LASER EXPERIMENT).** R. A. French[1], B. A. Cohen[2], and J. S. Miller[3], [1]Department of Earth and Planetary Sciences, Northwestern University, Evanston, IL, 60208 (renee@earth.northwesten.edu), [2]NASA Marshall Space Flight Center, Huntsville, AL, 35812, [3]Qualis Corporation, Jacobs ESSSA Group, Huntsville, AL, 35806.

**Introduction:** The Potassium-Argon Laser Experiment (KArLE) is composed of two main instruments: a spectrometer as part of the Laser-Induced Breakdown Spectroscopy (LIBS) method and a Mass Spectrometer (MS) [1-2]. The LIBS laser ablates a sample and creates a plasma cloud, generating a pit in the sample. The LIBS plasma is measured for K abundance in weight percent and the released gas is measured using the MS, which calculates Ar abundance in mols. To relate the K and Ar measurements, the total mass of the ablated sample is needed but can be difficult to directly measure. Instead, density and volume are used to calculate mass, where density is calculated based on the elemental composition of the rock (from the emission spectrum) and volume is calculated by pit morphology.

This study aims to reduce this uncertainty for KArLE by analyzing pit volume relationships in several analog materials and comparing methods of pit volume measurements and their associated uncertainties.

**Methodology:** A total of 11 samples with 5 possible Martian analog compositions (basalt, jarosite, rhyolite, microcline, and tuff) were prepared by cutting an analysis surface and polishing to 1 μm. These compositions provide a range of hardness, heterogeneity, porosity, and grain size.

We created a series of pits in each sample by firing the LIBS laser for a known number of shots, varying from 50 to over 1000 shots per pit. The pit geometry and volumes were determined using a Keyence VK-X100 laser scanning microscope, utilizing both laser scanning and optical imaging techniques. Platinum tubes manufactured by Johnson Matthey Medical were used to test volume measurement error of the Keyence and operator, resulting in an average error of 5%.

**Results:** Average pit volume (three measurements per pit) for 50 to 1350 LIBS shots per pit was calculated for a total of eight samples: basalt (four total with a range of grain sizes), jarosite, microcline (two total), and rhyolite. Figure 1 shows average pit volume as a function of number of LIBS shots per pit for each sample. Jarosite and rhyolite are heterogeneous and/or porous samples and display nonlinear volume increase. Linear volume increases are observed for basalt and microcline. Although some samples are heterogeneous (like some basalt), they still behave fairly linearly because their heterogeneity is on a similar scale as the laser pit. Slopes of best fit lines for basalt and microcline (Fig. 1) are less than half those for jarosite and rhyolite and exhibit greater $R^2$ values, possibly suggesting similarities between materials.

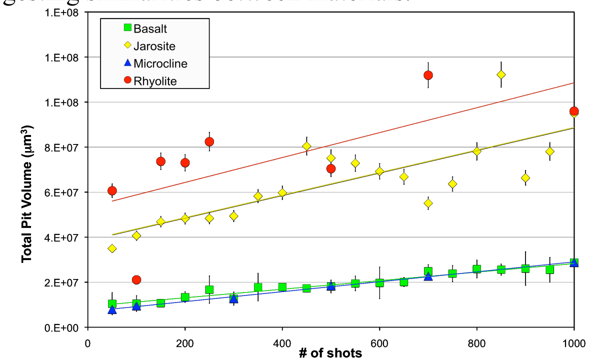


*Figure 1*: Average pit volume as a function of number of LIBS shots per pit for various sample compositions.

*Volume ablated per LIBS shot:* Average volume ablated per LIBS shot is displayed in Figure 2. This shows that although softer material forms deeper pits for the same number of LIBS shots than harder material, there is an exponential trend for all materials that can be fairly well predicted if the relative hardness is known or estimated (e.g., the Specific Grind Energy based on the energy expended per volume removed using the MER Rock Abrasion Tool).

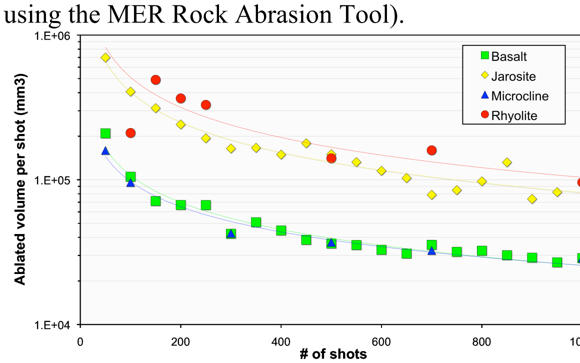


*Figure 2*: Average volume ablated per LIBS shot as a function of number of LIBS shots per pit.

*Pit reconstruction (Z-stacking):* We conducted optical image analysis of several pits using the optical mode of the Keyence microscope and the Olympus SZX16 stereomicroscope to understand how volume could be determined using the z-stacking method. A set of images was captured at fixed depth intervals and the in-focus part of the pit in each image was traced to create a contour map of pit morphology. Using this reconstruction, the contour areas and corresponding depth were used to calculate pit volume by summing the volume for each interval.

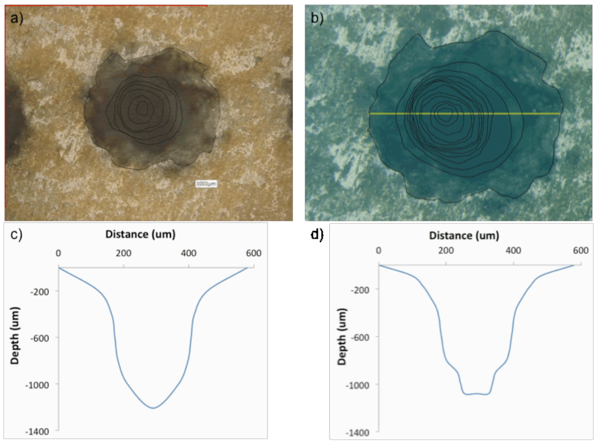


*Figure 3*: Reconstruction of Jarosite Sample 2 500 shots pit using the Keyence VK-X100 optical microscope (a and c) and Olympus SZX16 stereomicroscope (b and d). X-Y resolution for (a) is 1.39 um/pixel and for (b) is 0.19 um/pixel.

Figure 3 shows an example reconstruction for a pit in the jarosite sample generated with 500 LIBS shots. The reference volume using the Keyence laser microscope for this pit is 7.51E+07 $\mu m^3$. With the Keyence microscope, a total of seven layers over a depth of 1209 µm were stacked to reconstruct the pit (Fig. 3a) with a calculated volume of 8.93E+07 $\mu m^3$. With the Olympus stereomicroscope, we recovered thirteen layers over a depth of 1080 µm (Fig. 3b) and a calculated volume of 6.24E+07 $\mu m^3$. Both calculated volumes agree within 20% of the reference volume.

A second method for optically determining pit volume is by acquiring a pair of images with a slight offset from each other, enabling generation of a stereo pair and terrain mesh. We investigated this option using a stereo model and characteristics of the MAHLI camera on Curiosity (Ross Beyer, pers. comm.). We downsampled our data from the Keyence scanning microscope to the post spacing of the model. For each pixel, we calculated the volume to the reference surface as a simple prism under each pixel. This method gives a more accurate result than the z-stacking method, generally within 10% of the Keyence laser microscope-determined volume.

*Functional fits*: Finally, we considered a case where only minimal measurement capability might be available (e.g., pit depth and width). We determined parameterized fits to cross-sectional forms for pits in different materials and found that although a hyperbolic tangent is the best-fit shape for pit morphology, the number of free parameters exceeds the minimum measurements. A Gaussian fit is better using only these simplified parameters, but does not match pit morphology as well. Overall, volumes based on functional fits underestimate pit volume and introduce an uncertainty of about 30% into volume determination.

**Discussion**: Critical to the success of the KArLE experiment, or any LIBS-MS geochronology investigation [e.g., 3-4], is the accurate measurement of the LIBS-ablated pit. This study shows that either z-stacking or stereo imaging using available microimaging cameras are suitable methods for determining the volume of LIBS pits in flight designs (Fig. 4). In a pinch, material properties (hardness, heterogeneity, porosity, and grain size) can be used to estimate the likely range of pit volume per shot and a functional fit using pit width and depth can estimate the pit volume within a larger uncertainty.

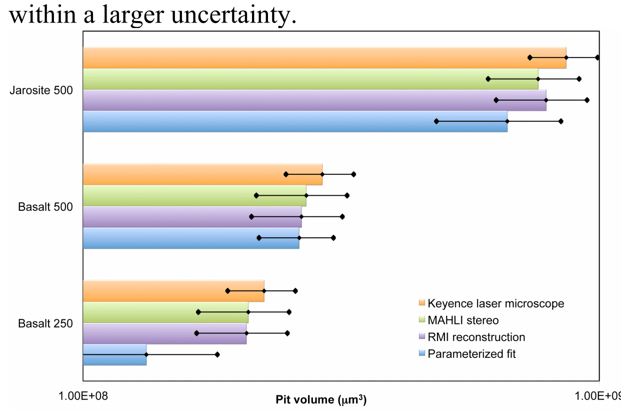


*Figure 4:* Comparison of volume calculation methods.

**References**: [1] Cohen B. A. et al. (2013) *LPSC XLIV,* Abstract #2363. [2] Cohen B. A. et al. (2012) Int'l Workshop on Instru. for Planetary Missions, Abstract #1018. [3] Cho Y. et al. (2012) Int'l Workshop on Instru. for Planetary Missions, Abstract #1093. [4] Devismes D. et al. (2013) European Planetary Science Congress 8, Abstract EPSC2013-2071.