CONTINUED DEVELOPMENT OF IN SITU GEOCHRONOLOGY FOR PLANETARY USING KARLE (POTASSIUM-ARGON LASER EXPERIMENT).

D. Devismes, B. A. Cohen, NASA Marshall Space Flight Center, Huntsville AL 35812 (barbara.a.cohen@nasa.gov)

Introduction: Geochronology is a fundamental measurement for planetary samples, providing the ability to establish an absolute chronology for geological events, including crystallization history, magmatic evolution, and alteration events, and providing global and solar system context for such events. The capability for in situ geochronology will open up the ability for geochronology to be accomplished as part of lander or rover complement, on multiple samples rather than just those returned. An in situ geochronology package can also complement sample return missions by identifying the most interesting rocks to cache or return to Earth.

The K-Ar radiometric dating approach to in situ dating has been validated by the Curiosity rover on Mars as well as several laboratories on Earth. Several independent projects [1-4] developing in situ rock dating for planetary samples, based on the K-Ar method, are giving promising results. Among them, the Potassium (K)-Argon Laser Experiment (KArLE) at MSFC is based on techniques already in use for in planetary exploration, specifically, Laser-induced Breakdown Spectroscopy (LIBS, used on the Curiosity Chemcam), mass spectroscopy (used on multiple planetary missions, including Curiosity, ExoMars, and Rosetta), and optical imaging (used on most missions).

Methodology: Using LIBS, a laser ablates the rock and creates a plasma, whose spectrum yields elemental abundances, including K. The ablated material frees gases, including radiogenic ^{40}Ar, which are let into a mass spectrometer (MS). The potassium and ^{40}Ar are related by the ablated mass. The mass is calculated using the ablated volume (Fig. 1) and the density of the material. The determination of the chemistry, and therefore the mineralogy, is provided by the LIBS spectra, enabling the density to be determined. The volume of the pit is measured using optical imagery.

Our component-level proof-of-concept tests and our end-to-end KArLE experiments on analog samples bring the KArLE experiment to Technology Readiness Level (TRL) 4, measuring a whole-rock K-Ar age with 10% uncertainty or better for rocks 2 Ga or older, sufficient to resolve the absolute age of many planetary samples and in line with expectations set by NASA Space Technology Roadmaps. However, one of the largest sources of uncertainty is the volume measurement.

We have previously investigated optical imaging as a volume solution, including z-stacking a set of images at decreasing focal planes and stereo imaging using available microimaging cameras; both are suitable for determining the volume of LIBS pits in a mission setting, meeting the targeted 10% uncertainty [5].

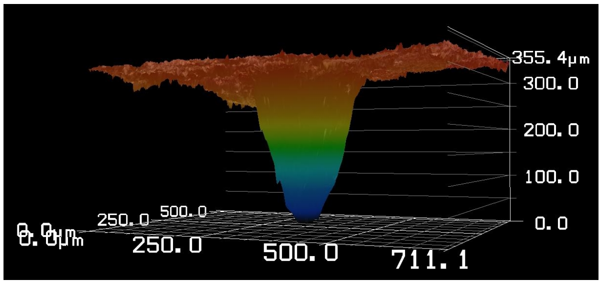

Figure 1: Ablated pit 500 pulses. 3D model made with microscope Keyence VK-100.

However, we may be able to take advantage of the LIBS instrument to help further constrain the ablated volume. The ultra-long ablation (hundreds of pulses) of the geologic sample under high vacuum (from 10^{-7} to 10^{-5} mbar) induces several effects on the LIBS spectra. One is that the continuum increases with the variation of geometry of the pit (1); another is that the material in the plasma plume plates out onto the surroundings in a measurable way (2). We have investigated whether these effects could be opportunistic options to estimate the ablated volume, either alone or in conjunction with optical imaging.

Results: *(1) Evolution of the continuum.* As LIBS ablation proceeds, the shape and magnitude of the background continuum changes in a regular way (Figure). This relation was previously described on geologic samples by [6], but under different conditions, with a continuum between 290 and 293 nm and for only 5 to 20 laser pulses. The number of pulses used for in situ geochronology is significantly larger, generally around 250 to 1000.

We created long-duration (250-1000 pulses) LIBS pits in a variety of homogeneous and heterogeneous planetary analog materials. For each pit, we correlated the difference of the intensity of the continuum between the first (shallowest) and the last (deepest) spectra with the volume measured with the laser microscope. The results give a linear correlation (Fig. 2).

A “homogeneous” pit merely means that the average material is the same throughout the experiment – the material may be mixed phases but in a constant ratio and small grain size, or they could be single minerals of different types, such as feldspar or pyroxenes. That the relationship holds regardless of the material and indicates that this technique could be widely applied on geologic samples.

The relative standard deviation (RSD) of this method begins to be valuable (less than 15%) when the ablated volume is bigger than 6E10^6 µm^3. There is less than 10% of uncertainty for ablated volumes larger than 9E10^6 µm^3, meaning it may be directly implemented in the geochronology protocol. One of the benefits of this approach is the simplicity of the technique and the use of already existing data, which is valuable for an in situ experimental setup.

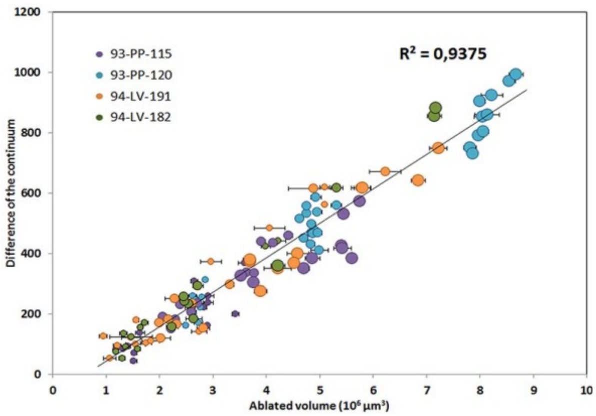

Figure 2: Correlation between the difference of the continuum and the ablated volume of 122 homogeneous pits from 4 samples with 3 different number of pulses.

(2) *Plasma deposits.* One of the consequences of LIBS is the production of plasma deposits (PD) due to plating out of the material displaced during laser ablation (Fig. 3).

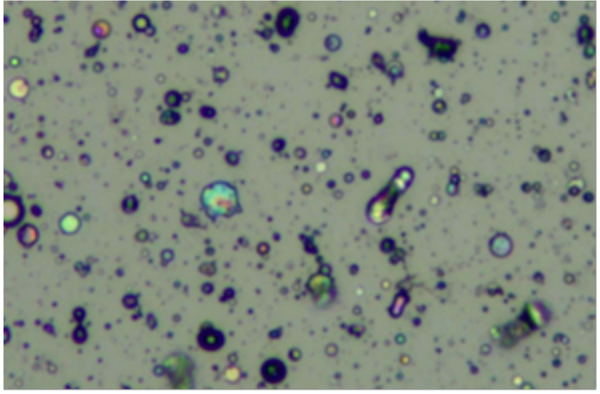

Figure 3: Plasma deposit on a glass slide from a basalt ablated by 50 pulses with a laser fluence of ~3GW/cm². The angle between the target and the laser beam is about 8°. The width of the picture is 100 µm.

As the sample is under high vacuum, the plasma has a stable conic dispersion which induces a regular distribution of the PD. Integrated in the vacuum chamber, few centimeters above the plasma along the laser beam, a Quartz Crystal Microbalance (QCM) could be the solution to directly estimate the ablated mass. Assuming that a constant a fraction of PD will deposit on the sensor, after calibration we could measure the deposit and relate it to the ablated mass. The QCM has several advantages: it is a miniaturized and flight proven instrument, it is also very sensitive as it has a mass sensitivity of 10^{-11} g.cm^{-2}.s^{-1}.

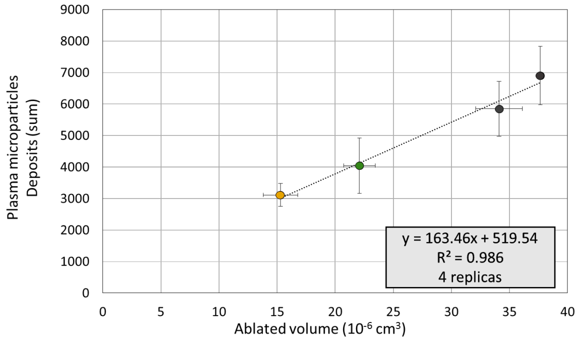

Figure 4: Correlation between the sum of the PD (size >1µm) and the ablated volume from a basalt sample.

Based on the study of the PD distribution of on glass, preliminary studies show a good reproducibility of the pattern of the plasma deposits coming from different ablated basalts (Fig. 4). We will continue to investigate the reproducibility of the PD patterns between different rocks and minerals. If the method has an accuracy of better than 10% on the ablated mass, we can reasonably think that this innovative approach could be integrated into future prototypes.

Future work: These new methods will be enhanced by more experiments on different samples and numerical models (e.g. to determine the best position for the QCM). Using these methods as complements to the LIBS-MS-microscope approach, we hope to provide faster and better measurements of the ablated mass as well as the age of the rock.

References: [1] Cohen et al. (2014) *Geostandards and Geoanalytical Research*, [2] Cho et al. (2011) *PERC Planetary Geology Field Symposium*, Abstract #30, [3] Devismes et al. (2013) *EPSC 2013*, Abstract #2013-71, [4] Farley et al. (2013a) *Geochimica et Cosmochimica Acta*, [5] French et al. (2014) *XLV*, Abstract #1936, [6] Lazic et al. (2001) Spectrochim. Acta Part B.

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