Continued development of in situ geochronology for planetary missions using KArLE (Potassium-Argon Laser Experiment)

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Why?
One of the most important pieces of data we need to acquire on planetary surfaces is their absolute age. Without sample returns, we can only estimate the age of many surfaces with crater counting. The uncertainty in these estimates in absolute ages can be considerable. KArLE is a LIBS-MS approach to in situ dating that could be carried on rovers to the Moon, Mars, etc.

What are the goals?
In situ age dating using LIBS-MS techniques requires the ablated mass, usually calculated by the sample density per ablated volume. We are investigating alternatives that may be able to estimate ablated mass with better precision and/or simpler techniques.

Estimation of ablation pit mass:
Rock density does not vary over a wide range; typical ablated volumes range from 5 to 80 $10^{-6}$ $\mu$m$^3$. To measure volume, several approaches have been studied. Optical imaging (stereo-imaging, z-stacking) uses flight-proven cameras to measure the volume. This approach yields volume measurements with 15%. We are investigating alternative approaches to improve the accuracy and precision, or at least provide complementary information to the optical imaging.

1. The relationship between the ablated volume and the LIBS continuum.
2. The in situ direct measurement of the ablated mass with a Quartz Crystal MicroBalance (QCMB).

Evolution of the LIBS spectra continuum during ablation

First described by Lazic et al. (2004), there is a relationship between the ablated volume and the LIBS continuum. We are investigating the extent to which it is feasible to estimate the volume by quantifying the variation of intensity of the continuum. Because this is a matrix-dependent effect, we are investigating it across a range of analog samples.

In aphanitic (fine-grained) basaltic, there is a good correlation between the 'difference of the continuum' and the ablated volumes. The relationship holds for different durations of ablation (shown are 250, 500, or 1000 pulses).

Ablated volumes >8 $10^{-6}$ $\mu$m$^3$ have a relative uncertainty <1% and volumes larger than 9 $10^{-6}$ $\mu$m$^3$ have a relative uncertainty better than 1%.

Plasma-deposited mass with a QCMB:
As the LIBS ablates the sample, material is scattered more or less spherically. Material plated onto a QCMB head may be proportional to the total amount of material that participated in the ablation.

The relation between the amount of plasma deposit particles counted and the ablated volume measured gives a very promising relationship.

The QCMB is a sensitive, flight-proven instrument (Dawn, Rosetta) that may be useful in measuring the mass participating in LIBS ablation. Assuming an optimal position and orientation, the fraction of particles collected by the sensor should be constant. Thus this approach may allow estimation of the ablated volume with a promising accuracy and precision.

Conclusions
Since these techniques are very new and as they have never been used for this purpose, they will need to be replicated by several independent studies. These techniques may be very important if the optical imaging encounters difficulties, for example, if a sample is made of very dark or monochromatic material and in the case of very deep pits (>500 $\mu$m).

Based on the preliminary results, the LIBS-continuum technique is more appropriate to the large pits produced by long ablutions. The relationship may work best for homogeneous samples, but the continuum is collected with every LIBS analysis and so does not require any addition to the experimental suite of techniques.

The integration of a QCMB in the ablation chamber may be a very interesting solution to determine the ablated mass. Even if it only measures a fraction of the total mass, its sensitivity should be able to weigh hundreds of nanograms accumulated on the crystal during ablation and relate it to the actual ablated mass.

In the future, these options may help in situ K-Ar dating to give the age of the rock with the best accuracy and precision.