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RELATIONSHIP BETWEEN LIBS ABLATION AND PIT VOLUME FOR GEOLOGIC SAMPLES: APPLICATIONS FOR IN SITU ABSOLUTE GEOCHRONOLOGY

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1 Why?

One of the most important pieces of data we need to acquire on Mars is the absolute age of its surface. Currently, we can only estimate the age of the surface with crater counting. The uncertainty in these estimates in absolute ages can be considerable, particularly for surfaces 2-3 Ga.

What are the goals?

In situ age dating using LIBS-MS techniques
Measurement error in LIBS to 10% on K and other major elements
Measurement error in ablated volume to 10%
Combined age uncertainty to 10% on samples 2 Ga or older

$$t = \frac{1}{\lambda} ln\left[\frac{^{40}Ar^*}{^{40}K}\left(\frac{\lambda}{\lambda_e}\right)+1\right] \longrightarrow \frac{^{40}Ar^*}{\%K\ d\ V}$$

$^{40}Ar^*$: Quadrupole mass spectrometry (QMS)
%K: Laser Induced Breakdown Spectroscopy (LIBS)
d (density): Chemistry of the sample (LIBS)
> V (ablated volume): Reproducibility, optical imaging, LIBS spectra

t = age
λ = total decay constant of ^{40}K
$λ_e$ = decay constant of ^{40}K to ^{40}Ar

d x V = ablated mass

2 Options to measure/estimate *in situ* the ablated volume

(1) Reproducibility of ablation

Hypothesis: In the same conditions of ablation, the ablated volume of a characterized mineral or chemistry (via the LIBS spectra) is reproducible. So based on a laboratory database, we should be able to estimate the ablated volume of the *in situ* measurement.

Problem: This hypothesis should be efficient for metals but it may be more difficult for geological materials. More than that, the accuracy of this method could be lower than expected. It also needs a very accurate description of the ablated minerals.

First results: Homogeneous groundmass and millimeter size minerals are the best targets to get a good reproducibility of the ablated volume. However depending on the rocks, several pits of ablation are heterogeneous and so reduce the interest of this method.

(2) Optical imaging

Method: The technics used are z-stacking and stereo-imaging. The currently-flying instruments available are the MER Microscopic Imager (MI), Curiosity Mars Hand Lens Imager (MAHLI), and Curiosity Remote Microimager (RMI)

Feasibility: Pit volume measurements for in situ geochronology is feasible on rovers/landers with existing flight-tested technology. (French et al., 2014)

Uncertainties: The previous studies show that the accuracy of this method is ~10%.

MAHLI camera

(3) LIBS Spectra

Hypothesis: LIBS spectra acquired under high vacuum record several trends due to the variation of pressure and of the crater's geometry on the peaks and on the continuum. So the spectra may rely to the ablated volume.

Advantage: LIBS spectra already give the %K and the chemistry/mineralogy of the ablated material. They could also help to give the ablated volume.

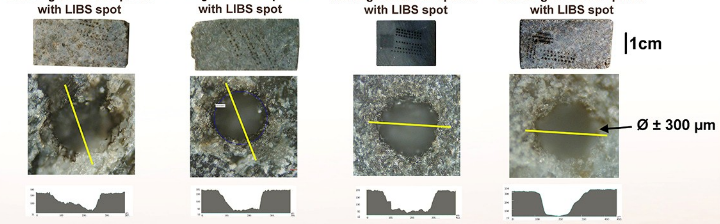
Uncertainties: The hypothesis has to be confirmed and the uncertainties need to be determined.

> This poster shows the preliminaries results of this approach.

3 Samples

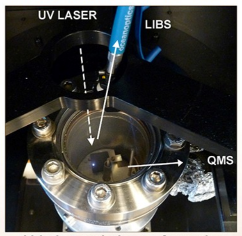
Dioritic and basaltic sill samples from the Dry Valleys, Antarctica (courtesy B. Marsh)
Dominant mineralogy: pyroxene and feldspar / Variable grain sizes

94-LV-191	93-PP-115	93-PP-120	94-LV-182
Mean grain size: 2-4 mm Coarse-grained compared with LIBS spot	Mean grain size: nx10 µm Fine-grained compared with LIBS spot	Mean grain size: n µm Homogeneous compared with LIBS spot	Mean grain size: 1- 4 mm Coarse-grained compared with LIBS spot

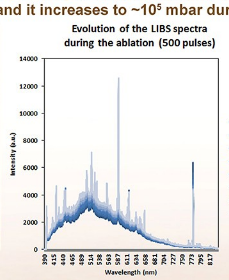


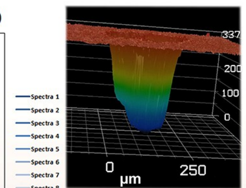
4 Experimental setup (Univ. Paris Sud)

Laser Q-switched Spectra Physics Nd-YAG / Pulsewidth : 14ns / 10 Hz / Wavelength : 266 nm / P laser : 0.1 W / Irradiance : ~3GW/cm² / lens f : 0.25
Ocean Optics HR2000+ / Spectral range : 385-850nm / Spectral resolution : 0.21-0.23nm / achromatic lens distant from 10cm (~vertical) to the plasma with a 1000µm Premium fiber
Sample of basalt / igneous rocks analog to the martian rocks (chemistry and/or Ar/g)
The pressure is at ~10^{-7} mbar and it increases to ~10^{5} mbar during the ablation



Ablation and plasma formation under high vacuum (10^{-7} mbar)





Ablated volume measured by Keyence microscope X100

5 Method - Sorting

¤ 4 different samples with tens of ablations at 250 / 500 / 1000 pulses.

¤ LIBS spectra are acquired during 1 second and averaged 5 times (giving respectively ~5 / ~10 / ~15 spectra per ablated pits).

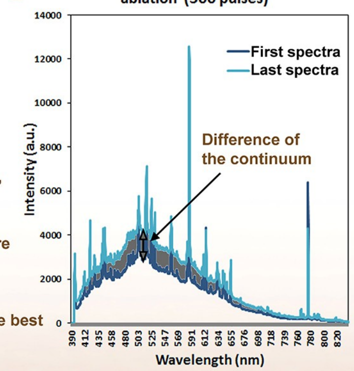
¤ LIBS spectra are corrected from the dark and from the continuum.

¤ Peaks of the studied elements: K at 766nm, Ca 422nm, Fe 429nm, Mg 518nm, Na 588nm and O 777nm.

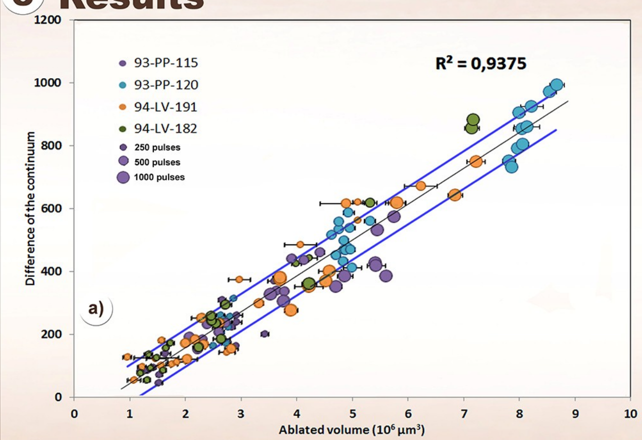
¤ Only the pits with homogeneous spectra are kept (122 on 177 ablated pits).

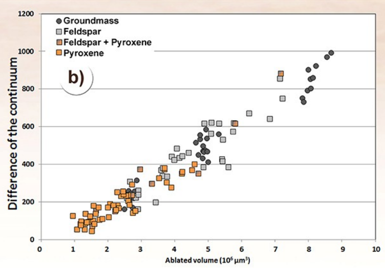
The comparison of all the data with the measured ablated volume has shown that the best correlation is between the «difference of the continuum intensity» vs volume.

First and last LIBS spectra of the ablation (500 pulses)

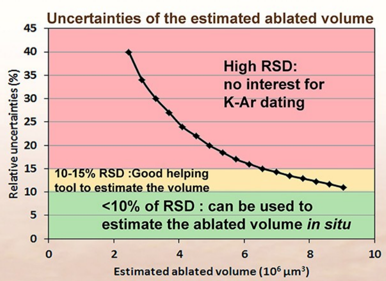


6 Results





Correlation between the 'difference of the continuum' and the ablated volumes of 122 homogeneous pits from 4 samples ablated with 250, 500 or 1000 pulses (a) and with several mineralogies: pyroxenes, feldspars, mixes of pyroxenes and feldspars, groundmass (b). The blue curves are the prediction at 1 sigma.



Only by sorting the homogeneous pits via their LIBS spectra, there is a strong correlation between the ablated volumes and the 'difference of the continuum'.

This method can be used whatever the mineralogy or the duration of the ablation are.

The uncertainties of this correlation give an estimated volume with less than 15% of RSD when the volume is higher than $6.10^6 µm^3$.

Under 15% of uncertainties, this method is an interesting tool to complete the direct measurement of the ablated volume.

And if we ablate bigger volumes, the uncertainties will be under 10%. It is enough to give the age of the rock with few uncertainties.

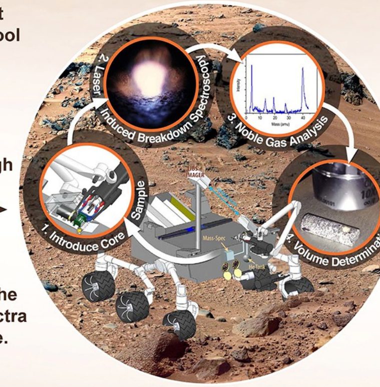
7 Conclusion - Future work

These firsts results demonstrate that LIBS spectra can be an interesting tool to estimate the ablated volume.

When the ablated volume are bigger than $9.10^6 µm^3$, this method has less than 10% of uncertainties. Far enough to be directly implemented in the KArLE experiment protocol.

Nevertheless, depending on the samples and their mean grain size, the difficulty to have homogeneous spectra will increase with the ablated volume.

Several K-Ar dating studies based on this approach will be implemented. After that, the results will be shown and discussed.



The Potassium Argon Laser Experiment (KArLE) concept. Cohen et al. (2014)