

## Relationship between LIBS ablation and pit volume for geologic samples: Applications for in situ absolute geochronology.

In planetary sciences, in situ absolute geochronology is a scientific and engineering challenge. Currently, the age of the Martian surface can only be determined by crater density counting. However this method has significant uncertainties and needs to be calibrated with absolute ages.

We are developing an instrument to acquire in situ absolute geochronology based on the K-Ar method. The protocol is based on the laser ablation of a rock by hundreds of laser pulses. Laser Induced Breakdown Spectroscopy (LIBS) gives the potassium content of the ablated material and a mass spectrometer (quadrupole or ion trap) measures the quantity of  $^{40}\text{Ar}$  released. In order to accurately measure the quantity of released  $^{40}\text{Ar}$  in cases where Ar is an atmospheric constituent (e.g., Mars), the sample is first put into a chamber under high vacuum. The  $^{40}\text{Ar}$  quantity, the concentration of K and the estimation of the ablated mass are the parameters needed to give the age of the rocks. The main uncertainties with this method are directly linked to the measures of the mass (typically some  $\mu\text{g}$ ) and of the concentration of K by LIBS (up to 10%).

Because the ablated mass is small compared to the mass of the sample, and because material is redeposited onto the sample after ablation, it is not possible to directly measure the ablated mass. Our current protocol measures the ablated volume and estimates the sample density to calculate ablated mass. The precision and accuracy of this method may be improved by using knowledge of the sample's geologic properties to predict its response to laser ablation, i.e., understanding whether natural samples have a predictable relationship between laser energy deposited and resultant ablation volume. In contrast to most previous studies of laser ablation, theoretical equations are not highly applicable. The reasons are numerous, but the most important are: a) geologic rocks are complex, polymineralic materials; b) the conditions of ablation are unusual (for example, variable vacuum pressure), and c) the ablation is made with hundreds of successive laser pulses. In this work, we aim to understand the effects that occur on LIBS spectra when a homogeneous rock or a mineral is ablated under high vacuum.

Understanding these effects is important to define best practices for LIBS measurements and may lead to improved measurement (or possibly prediction) of the ablated volume. We will describe our laboratory approach and first results, and discuss its utility for in situ absolute geochronology campaigns.