

UPDATES OF THE KARLE EXPERIMENT: NEW LIBS CALIBRATION UNDER HIGH VACUUM FOR THE QUANTIFICATION OF POTASSIUM IN BASALT FOR IN SITU GEOCHRONOLOGY. D. Devismes¹, B. A. Cohen¹, Z.-H. Li^{1,2}, J. S. Miller^{1,3}. ¹NASA Marshall Space Flight Center, Huntsville AL 35812 (damien.p.devismes@nasa.gov), ²University of Alabama Huntsville, Huntsville AL 35805; ³Qualis Corporation, Jacobs ESSSA Group, Huntsville AL 35806.

Introduction: In planetary exploration, in situ absolute geochronology is one of the main important measurements that needs to be accomplished. Until now, on Mars, the age of the surface is only determined by crater density counting, which gives relative ages. These ages can have a lot of uncertainty as they depend on many parameters. More than that, the curves must be ties to absolute ages. Thus far, only the lost lander Beagle 2 was designed to conduct absolute geochronology measurements, though some recent attempts using MSL Curiosity show that this investigation is feasible and should be strongly encouraged for future flight.

Experimental: The Potassium (K)-Argon Laser Experiment (KARLE) is being developed at MSFC through the NASA Planetary Instrument Definition and Development Program (PIDDP). The goal of this experiment is to provide in situ geochronology based on the K-Ar method. A laser ablates a rock under high vacuum, creating a plasma which is sensed by an optical spectrometer to do Laser Induced Breakdown Spectroscopy (LIBS). The ablated material frees gases, including radiogenic ⁴⁰Ar, which is measured by a mass spectrometer (MS). As the potassium is a content and the ⁴⁰Ar is a quantity, the ablated mass needed in order to relate them. The mass is given by the product of the ablated volume by the density of this material. So we determine the mineralogy of the ablated material with the LIBS spectra and images and calculate its density. The volume of the pit is measured by using microscopy.

LIBS measurement of K under high vacuum: Three independent projects [1, 2, 3] including KARLE, are developing geochronological instruments based on this LA-LIBS-MS method. Despite several differences in their setup, all of them have validated the methods with analyses and ages. However, they all described difficulties with the LIBS measurements of K [3,4].

At ambient pressure, the quantification of K by LIBS on geological materials can be accurate [5]. However the protocol of the LA-LIBS-MS experiment required hundreds of shots under high vacuum in order to free enough ⁴⁰Ar* to be measured by the QMS. This long duration of ablation may induces significant changes in the LIBS spectra. The pressure may increases by orders of magnitude within the chamber and the laser pit geometry can change the effectiveness of

ablation and intensity of plasma light received. These effects introduce variation between the first and last spectra and so the quantification of K is more complex. The ablation of one crater can give, depending on the protocol of acquisition, from tens to hundreds of spectra.

Protocol and results: We are in the process of further characterizing the variation introduced into LIBS spectra by the use of hundreds of laser shots, and defining a protocol that can be used to ensure accuracy and reproducibility in the results. We are using natural rock powder standards fused in a furnace, as well as mars analog samples with known K content. We will show the result of the calibration and some new statistical approaches in order to apprehend the effects of the long time ablation on rocks under high vacuum.

Upcoming work: The next step will be to optimize the measurement of the ablated volume. The ablation of rocks in high vacuum with hundreds of laser pulses produces craters deep of hundreds of μm . The shape of the crater depends on many different parameters, including the optical setup and the size of the microcrystals of the groundmass. We are working on protocols [6] which should be able to produce accurate measurements of these volumes. By doing this on a large collection of well-known samples, we expect to have a better understanding of the effects of extended ablation of rocks under high vacuum.

References: [1] Cho et al. (2011) *PERC Planetary Geology Field Symposium*, Abstract #30. [2] Cohen et al. (2012) *LPS XLIII*, Abstract #1267. [3] Devismes et al. (2013) *EPSC 2013*, Abstract #2013-71. [4] Cho et al. (2013) *LPS XLIV*, Abstract #1505. [5] Stipe et al. (2013) *Spectrochimica Acta Part B: At. Sp.*, 70, 45-50. [6] French et al. (2014) *XLV*, Abstract #1936.

Acknowledgement: This research was supported by an appointment to the NASA Postdoctoral Program at the Marshall S.F.C., administered by Oak Ridge Associated Universities through a contract with NASA.