

Continued development of in situ geochronology for planetary missions

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Abstract

The instrument ‘Potassium (K) Argon Laser Experiment’ (KArLE) is developed and designed for *in situ* absolute dating of rocks on planetary surfaces. It is based on the K-Ar dating method and uses the Laser Induced Breakdown Spectroscopy – Laser Ablation – Quadrupole Mass Spectrometry (LIBS-LA-QMS) technique. We use a dedicated interface to combine two instruments similar to SAM of Mars Science Laboratory (for the QMS) and ChemCam (for the LA and LIBS). The prototype has demonstrated that KArLE is a suitable and promising instrument for *in situ* absolute dating.

1. Introduction

In planetary exploration, *in situ* absolute geochronology is an important measurement. Thus far, on Mars, the age of the surface has largely been determined by crater density counting, which gives relative ages. These ages can have significant uncertainty as they depend on many poorly-constrained parameters. More than that, the curves must be corrected with absolute ages to relate geologic time-scales on Mars to the rest of the solar system. 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 [1] and should be strongly encouraged for future flight.

2. Experimental

Developed at NASA MSFC through the NASA Planetary Instrument Definition and Development Program (PIDDP), KArLE is one of several projects working on in situ geochronology [2, 3, 4]. The protocol is based on several instruments already used in planetary exploration. Using Laser Induced Breakdown Spectroscopy (LIBS), a laser ablates a

rock under high vacuum and creates a plasma, whose spectrum yields elemental abundances, including K. The ablated material frees gases, including radiogenic ^{40}Ar , which is measured by a mass spectrometer (MS). The potassium and ^{40}Ar are related by the ablated mass. Because the very small mass displacement cannot be easily measured directly, the mass is calculated using the ablated volume and the density of the material. The determination of the chemistry, and therefore the mineralogy, is provided by the LIBS spectra and their treatment (univariate calibration, Partial Least Square, etc.) enabling the density to be determined. The volume of the pit is measured using optical imagery, for example, stereo imaging or focal plane stacking.

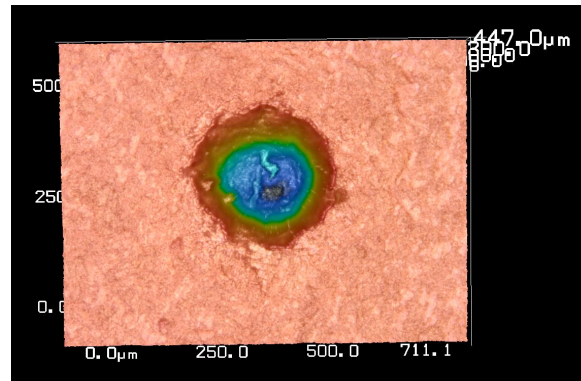


Figure 1: Ablated pit after 1000 pulses. 3D model made with Keyence microscope VK-X100.

3. Recent studies and future upgrades

The LIBS-MS method for in situ K-Ar dating has been demonstrated with several prototypes in independent laboratories [2, 3, 4 and 5]. As a very new technique, we need to explore the effects induced by the ultra-long ablation under high vacuum on the results and on the protocol [6], the

performance of the K measurement by LIBS [7] and the ability to estimate the ablated volume with the LIBS spectra [8]. These investigations and future studies will help enhance the performance of the instrument and determine more precise K-Ar ages.

As an example, we have been working on an approach for estimating pit volume based on LIBS spectra, specifically the evolution of the continuum intensity during the ablation. This relation was previously described on geologic samples by Lazic et al. [9], 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 Martian 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. 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 relation 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 $6 \times 10^6 \mu\text{m}^3$. There is less than 10% of uncertainty for ablated volumes larger than $9 \times 10^6 \mu\text{m}^3$, meaning it may be directly implemented in the geochronology protocol.

Based on these first results, this method may prove useful in confirming the measurements given by optical techniques. 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.

We are currently working on understanding the generation and expansion of the plasma cloud itself, to determine how material is distributed and condensed during the experiment. We are also working to implement the LIBS-MS technique using a ion-trap mass spectrometer (ITMS), a smaller and

lighter mass spectrometer than typical quadrupole mass spectrometers. The results of our ongoing work will also help to determine how best to implement a flightlike brassboard to increase the Technology Readiness Level (TRL). For example, we will enhance the protocol by matching parameters compared to ChemCam and SAM on MSL (e.g. laser power, laser pulse frequency, viewing geometry, etc.). We also expect to integrate in the prototype setup a flightlike design of the sample inlet and ablation cell, a new development for the future KARLE instrument.

Summary

We present new technological developments for in situ dating using the K-Ar approach and several results affecting future advancement. We will discuss results achieved using the KARLE setup and make recommendations for future in situ instrumentation.

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References

- [1] Farley, K. A., Malespin C., Mahaffy P. et al.: In Situ Radiometric and Exposure Age Dating of the Martian Surface. *Science*, 343(6169), 1247-1266, 2013.
- [2] Cohen, B. A., Miller, J. S., Li, Z.-H., Swindle, T. D. and French, R. A.: The Potassium-Argon Laser Experiment (KARLE): In Situ Geochronology for Planetary Robotic Missions. *Geostandards and Geoanalytical Research*, 38: 421–439, 2014.
- [3] Cho et al. (2011) PERC Planetary Geology Field Symposium, Abstract #30.
- [4] Devismes, D., Gillot, P.-Y., Lefèvre, J.-C. and Boukari, C.: A K-Ar development based on UV laser for in situ geochronology on the surface of Mars. Firsts results and isochrones. *European Planetary Science Conference*, 8, #2013-71, 2013
- [5] Solé J.: In situ determination of K–Ar ages from minerals and rocks using simultaneous laser-induced plasma spectroscopy and noble gas mass spectrometry. *Chemical Geology*, 388, 9-22 (2014)
- [6] Devismes, D., Cohen, B. A. and Gillot, P.-Y.: Developing a relationship between LIBS ablation and pit volume for in situ dating of geologic samples LPSC 2015, Abstract #1406.
- [7] Cho, Y., Sugita, S. et al.: High-precision potassium measurements using laser-induced breakdown spectroscopy

under high vacuum conditions for in situ K–Ar dating of planetary surfaces. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 106, 28-35, 2015.

[8] Devismes, D., Cohen, B. A. et al.: Relationship between LIBS ablation and pit volume for geologic samples: Applications for in situ absolute geochronology. *SciX*, Abstract #216