

**APPLICATION OF THE POTASSIUM-ARGON LASER EXPERIMENT (KArLE) TO ORDINARY CHONDRITES.** F. Cattani<sup>1,2</sup>, B. A. Cohen<sup>2</sup>, J. Olsson<sup>3</sup>. <sup>1</sup>Catholic University of America, Washington D.C.; <sup>2</sup>NASA Goddard Space Flight Center, MD, USA ([fanny.cattani@nasa.gov](mailto:fanny.cattani@nasa.gov)); <sup>3</sup>University of Gothenburg, Sweden.

**Introduction:** The history of a planet is preserved in the rocks and geological structures that compose it. Absolute chronology is needed in order to understand and define the geological events with precision, such as crystallization history, magmatic evolution, and alteration event. Several experimental setups using spot laser analyses have been developed to investigate the feasibility of *in situ* K-Ar dating in future landing planetary missions [1-6]. We present here results using our *in situ* K-Ar dating prototype developed at NASA GSFC, KArLE. It quantifies potassium content (K) by laser-induced breakdown spectroscopy (LIBS), argon (Ar) by quadrupole mass spectrometry (QMS), and the ablated mass by profilometry.

The precision and accuracy of the LIBS-MS approach have been successfully demonstrated on many terrestrial samples [1-6]. These samples have >1 wt.% K<sub>2</sub>O and young ages (< 2 Ga). For the Moon, lithologies that would benefit from *in situ* dating have less K<sub>2</sub>O and older ages, making their analysis more challenging. We are therefore working on extending our KArLE techniques and data analysis methods to older and more K-poor samples as better lunar analogs.

**Methods:** For this purpose, we analyzed an Enstatite-chondrite (Hvittis) and an Ordinary chondrite (Pultusk). Hvittis is classified EL6 and is mainly composed of enstatite (60vol% - <0.04% of K), troilite (18vol% - no K), plagioclase (13vol% - 0.7% of K), and melt clast (5vol% - enriched in troilite and plagioclase). The mineralogy of this chondrite is heterogeneous and the grain size is under 100 μm [7]. Pultusk is classified as H5 breccia and is composed of olivine, bronzite, kamacite, troilite, chromite - plagioclase assemblages, and felspathic glass [8].

In this study, the rock samples are ablated under high vacuum with a UV laser to create a plasma and ablate a specified amount of sample without significant argon diffusion. During the plasma cooling, the light emitted between 450 and 800 nm is focused on the optical spectrometers by optics. This light is analyzed and allowed to define the chemistry of the target. Working under high vacuum allows confining the gas released during the ablation. This gas is purified and sent to the QMS, which allows defining the number of Ar released during the laser ablation. Finally, laser confocal technology allows obtaining images with a large depth of field and detects the finest details in the sample shape data. That allows defining the shape and the volume of the pits obtained.

For the data reduction, we used univariate analysis to define a correlation between the LIBS signal intensity at 766 and 770 nm and a known concentration using calibration curves build from standard sample analyses. The chondrites in this study have very low K content, but there exist few low-K standards, so our curve is more sparse than we would like. Also, matrix effects can be an issue because of the comparison between powder standards and rock samples. In order to understand these issues, we analyzed a known rock standard (AMP3.8, an Archean amphibolite [1]) at the same time and under the same conditions as the chondrites. In this study, we also examined different ways to process the LIBS data to obtain the K abundance. Our LabVIEW process defines the peak areas at 766 nm and 770 nm using a trapezoidal law. PyHAT processing is a Python script developed by the ChemCam team [9], which defines the peak areas at 766 nm and 770 nm using the local minima and maxima law. We also developed a Matlab script that allows fitting a Lorentz function and applies a deconvolution process for the Fe peak interference at 766 nm for each K peak.

**KArLE Results:** We performed 73 laser ablations on the amphibolite and the chondrites (with 1200 laser pulses on each point) to yield a range of K<sub>2</sub>O content and construct isochrons using the York regression [10].

AMP3.8 is composed of amphibole and plagioclase; the plagioclase has a K content of 0.3wt.% and a reference age of 2052 ± 29 Ma [1]. The KArLE results on plagioclase phases show a K-Ar age of 1900 ± 410 Ma (2σ).

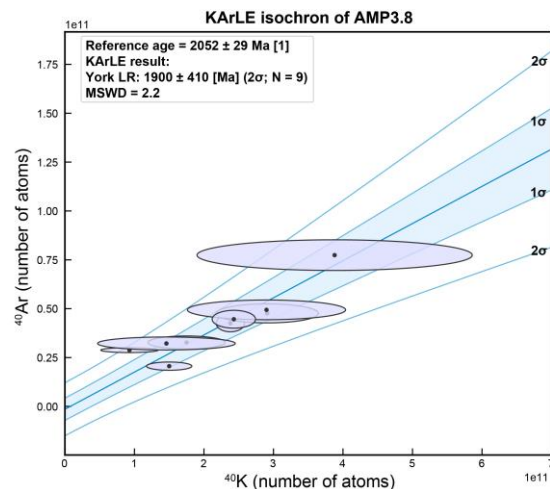


Fig. 1: KARLE results obtained on the amphibolite.

The LIBS results obtained on AMP3.8 had the best reproducibility and accuracy using the trapezoidal law for fitting the K peaks, so we used that method for the chondrite samples. The Hvittis sample has a bulk K content around 0.26wt.% but is very heterogeneous. Like all chondrites, it is composed of multiple phases that vary in K content and possibly in age and mode of formation. Nonetheless, a bulk Ar-Ar age has been measured at  $4547 \pm 6$  Ma [11]. We measured 43 points but only 8 of them had sufficient K content to be detected by our setup. Constructing an isochron using only the high-K points ( $> 0.07$  wt.% of K), the KARLE calculated age is  $4700 \pm 860$  Ma ( $2\sigma$ ).

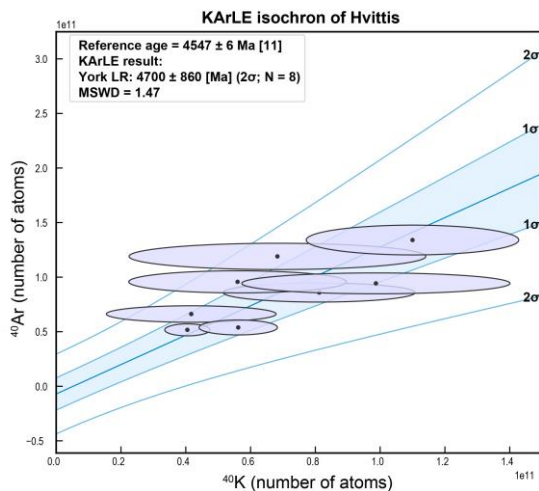


Fig.2: KARLE results obtained on Hvittis.

Pultusk has a very low K bulk content (under 0.1wt.%), and a Pb-Pb age defined at 4657 Ma [12]. Again, it is heterogeneous in its composition. We measured 21 points but avoiding the metallic, olivine, and bronzite phases (yellow areas), we selected 9 points with enough K to be detected. The KARLE calculated age is  $4600 \pm 880$  Ma ( $2\sigma$ ).

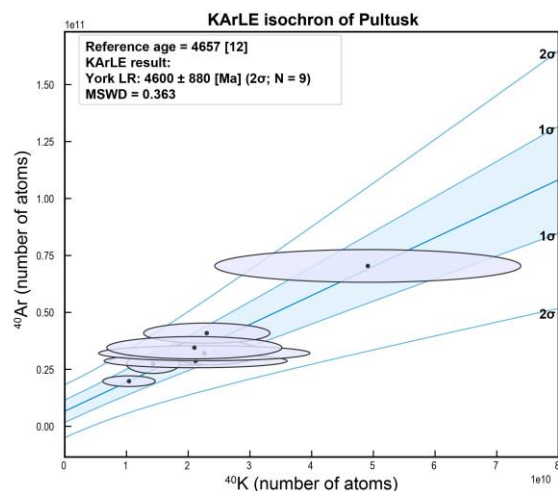


Fig.3: KARLE results obtained on Pultusk.

The results obtained from the laboratory KARLE yield K-Ar ages within the uncertainty of the reference age, and with a precision ( $2\sigma$ ) better than 20% for chondrite samples with K content at the LIBS quantification limit. We are not suggesting that KARLE is an appropriate technique for chondrites, but these results are encouraging for understanding the limits of the applicability of our technique and guiding future improvements for ancient planetary samples.

**Flight version:** The NASA's Development and Advancement of Lunar Instrumentation (DALI) program awarded funding to KARLE at NASA GSFC, to mature spacecraft-based instrument for use in future lander missions. Our team is building a KARLE brass board designed to minimize mass, volume, and power resources and raise the TRL maturity of all components. In particular, we are building a KARLE-specific sample handling carousel (with heritage from MSL SAM) and a miniaturized laser profilometer with heritage from similar device used on the International Space Station [13]. We expect to test and calibrate this miniaturized version in order to validate the readiness for flight on a small commercial lander/rover.

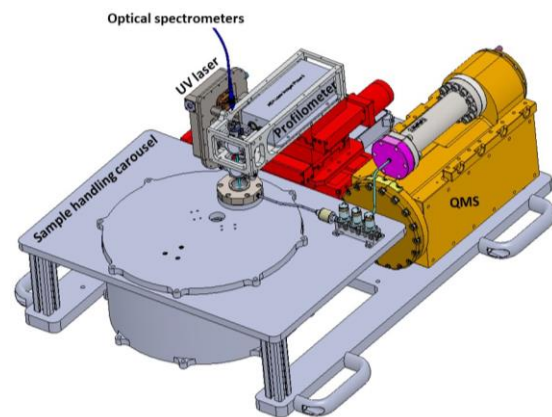


Fig.4: KARLE CAD model.

**References:** [1] Cattani F. et al. (2019) *Chem. Geol.* 506, 1-16. [2] Cohen B.A. et al. (2014) *Geostand. Geoanal. Res.* 38, 421-439. [3] Cho Y. et al. (2016) *Planet. Space Sci.* 128, 14-29. [4] Cho Y. and Cohen B.A. (2018) *Rap. Com. Mass Spectrom.* 32, 1755-1765. [5] Devismes D. et al. (2016) *Geostand. Geoanal. Res.*, 40, 517-532. [6] Solé J. et al. (2014) *Chem. Geol.* 388, 9-22. [7] Kinsey L.K. et al. (1995) *LPSC XXVI*. [8] Krzesinska A. and Fritz J. (2014) *Meteorit. Planet. Sci.* 49, 595-610. [9] Anderson R.B. et al. (2019) *4th Planetary Data Workshop*. [10] York D. et al. (2004) *Am. J. Phys.* 72(3), 367-375. [11] Bogard D.D. et al. (2010) *Meteorit. Planet. Sci.* 45.5, 723-742. [12] Tilton G.R. (1973) *Earth and Planet. Sci. Letters* 19, 321-329. [13] Samson C. et al. (2002) *SPIE Regional Meeting Opto-Canada*.