EXTENDING IN SITU DATING DEVELOPMENT TO LUNAR ROCKS USING THE POTASSIUM_ARGON LASER EXPERIMENT (KArLE). F. Cattani[1], B. A. Cohen[1], J. Olsson[2]. [1]NASA Goddard Space Flight Center, Greenbelt MD 20771 (fanny.cattani@nasa.gov); [2]University of Gothenburg, , Sweden.

Introduction: Absolute dating is needed to check and calibrate the relative chronology presently available from meteoritic crater counting. For that purpose, the K-Ar technique appears very promising as it is based on the radioactive decay of an isotope from a major element, potassium (K), which is often present in larger abundances than other radiometric parent elements, particularly for the Moon [1].

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 [2-7]. We present here an *in situ* K-Ar dating prototype developed at NASA GSFC, KArLE, an instrument based on laser ablation to vaporize a reproducible volume of rock or mineral. It quantifies potassium content (K) by laser-induced breakdown spectroscopy (LIBS), argon (Ar) by quadrupole mass spectrometry (QMS), and the ablated mass by profilometry (Fig. 1).

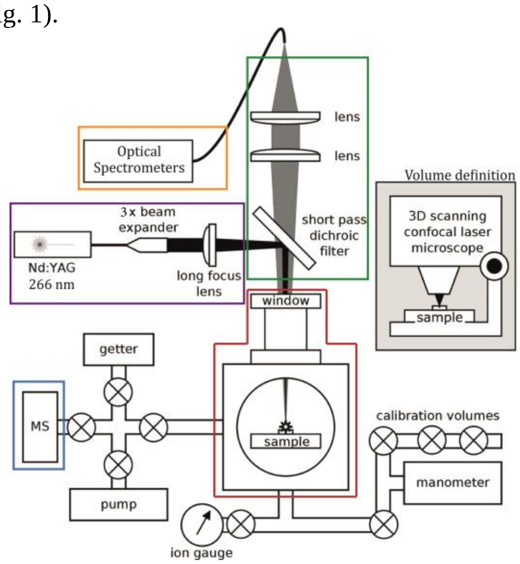

Fig.1: KArLE schema.

Calibration: We currently use univariate analysis to define a correlation between the LIBS signal and a known K concentration using calibration curves based on standard samples (rocks and minerals). The limit of detection (LOD) and the limit of quantification (LOQ) of K determinations are derived from these calibration curves (Fig. 2). Following the approach of Mermet [8], and using the weighted calibration at the 1σ confidence level, the LOD and LOQ in the current KArLE setup are 0.07 and 0.27 wt.%, respectively.

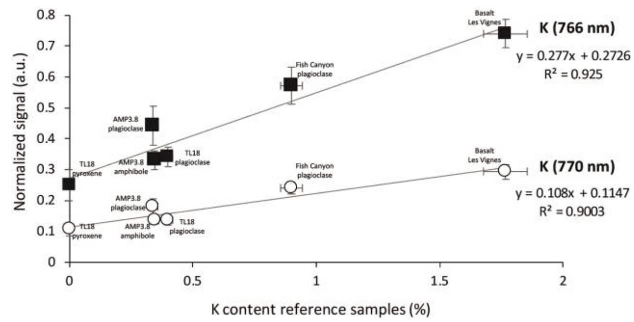

Fig.2: Calibration curves for the potassium doublet at 766nm and 770nm under vacuum conditions (10^{-9} Torr).

A very small amount of sample is evaporated during ablation (between 10 and 60µg), releasing radiogenic ^{40}Ar that is measured with an quadrupole mass spectrometer (QMS). The QMS detection limit in our current laboratory setup is around 5×10^{9} atoms for mass 40, with a corresponding uncertainty under 5%. Previous lab-work has confirmed the linearity of our QMS instrument in the range 1 to 20×10^{-9} Torr, corresponding to a range from 2×10^{8} to 4×10^{11} atoms of ^{40}Ar.

The precision and accuracy of the LIBS-MS approach have been successfully demonstrated on many terrestrial samples [2-7] (Fig. 3). In general, these samples have had >1 wt.% K_2O and young ages (<2 Ga). For the Moon, lithologies that would benefit from *in situ* dating (e.g., ancient basins, silicic volcanism, etc.) have less K_2O 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.

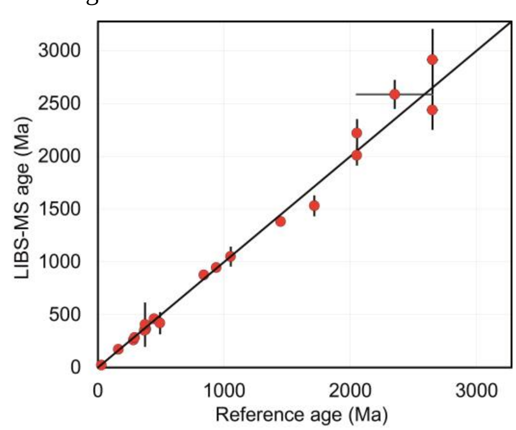

Fig.3: Compilation of the in-situ K-Ar ages obtained by different studies [2-7].

Results: Our first sample in our lunar campaign is Archaean amphibolite AMP3.8, composed of amphibole and plagioclase. The plagioclase has a K content of 0.3% and a reference age of 2052 ± 29 Ma; previous *in situ* K-Ar dating yielded its age as 2218 ± 135 Ma [9, 2]. We performed 19 UV laser ablations with 600 to 1800 laser pulses on the whole rock to yield a range of K_2O content and construct an isochron even when individual points scatter [10]. The KArLE calculated age is 2009 ± 96 Ma (1σ), within uncertainty of the reference age and with a precision better than 5% (Fig. 4).

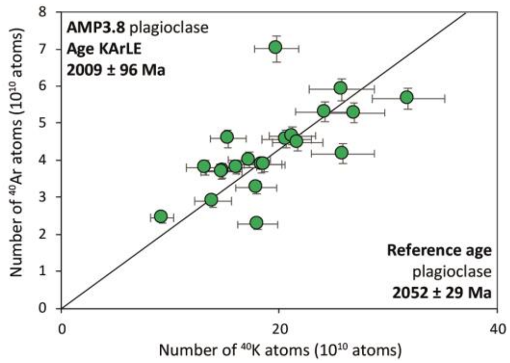

Fig.4: KArLE results obtained on plagioclases of AMP3.8.

Future work: The intensity of each elemental peak in a LIBS spectrum is not a simple function of elemental abundance; it is sensitive to the composition and crystal structure of the sample. Multivariate curve fitting techniques (such as Partial Least Squares, or PLS) will be used to understand the bulk composition of the sample and refine the K calibration curve better than univariate analysis [11]. We expect this technique to enable lower K contents to be measured, as well as being able to use the whole rock chemistry for context in the case of unknown samples. In addition, we are constructing a demultiplexer for our laboratory setup, similar to that in use by ChemCam and SuperCam, in order to improve the amount of light reaching each spectrometer over their respective wavelength ranges and further improve K measurements [12].

Another challenge is to determine the ablated mass, which depends on laser parameters, and on the mineral analyzed. For that purpose, and in order to build a device suitable for space applications, we are collaborating with NEPTEC, who will develop a miniaturized laser profilometer based on their Space Station instrument [13]. We will also continue working to understand the sensitivity of the laser pit volume to different parameters (e.g. mineral strength, density determination, color, shape, etc.) that affect the mass determination [2].

We will use these improvements to conduct analyses on higher-fidelity lunar analogs as well as planetary samples, including ordinary chondrites, Pultusk and Bjurböle (4.55 Ga and 4.46 Ga, respectively) [14], and lunar meteorite MET 01210 (3.90 Ga). Further experiments on meteorites and lunar samples like MET 01210 will illustrate the feasibility of the KArLE technique on the lunar surface.

Flight version: 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. Knowing the precise ages afforded through K-Ar dating would help scientists to check and calibrate the relative chronology presently available from meteoritic crater counting, and to understand the Moon's history, its formation, the effects of bombardment, and by extension, the history of the solar system.

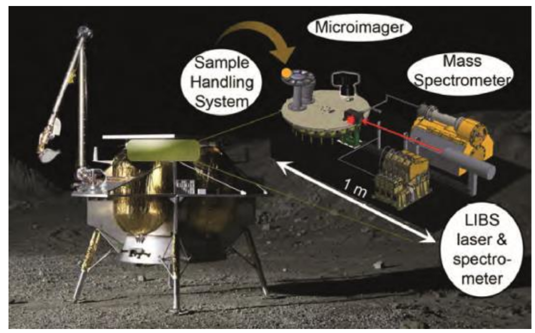

Fig.5: KArLE uses flight-heritage components to achieve the first in-situ geochronology of the Moon on a lander/rover (©Astrobotic).

We need to miniaturize KArLE and calibrate the instruments for the moon. Our team will build a high fidelity brass board to minimize mass, volume, and power resources, shown to satisfy all functional and science requirements. Then, we will test and calibrate this miniaturized version in order to validate the readiness for the flight on a small commercial lander/rover.

References: [1] Gast P.W. and Hubbard N.J. (1970) *Science, 167(3918)*, 485-487. [2] Cattani F. et al. (2019) *Chem. Geol. 506*, 1-16. [3] Cohen B.A. et al. (2014) *Geostand. Geoanal. Res. 38*, 421–439. [4] Cho Y. et al. (2016) *Planet. Space Sci. 128*, 14–29. [5] Cho Y. and Cohen B.A. (2018) *Rap. Com. Mass Spectrom. 32*, 1755–1765. [6] Devismes D. et al. (2016) *Geostand. and Geoanal. Res., 40*, 517–532. [7] Solé J. et al. (2014) *Chem. Geol. 388*, 9-22. [8] Mermet J.M. (2008) *Spectrochim. Acta B At. Spectrosc. 63*, 166–182. [9] David J. et al. (2009) *Geol. Soc. Am. Bull. 121*, 150-163. [10] Bogard D.D. (2009) *Meteorit. Planet. Sci., 44(1)*, 3-14. [11] Clegg S.M. et al. (2017) *Spectrochim. Acta B At. Spectrosc. 129*, 64-85. [12] Wiens R.C. et al. (2012) *Space Sci. Rev. 170(1-4)*, 167-227. [13] Samson C. et al. (2002) *SPIE Regional Meeting Opto-Canada*. [14] Olsson J. et al. (2020) *LPSC 51*.