# In-situ K-Ar dating based on UV-Laser ablation coupled with a LIBS-QMS system development, calibration and application


LPSC 50

Abstract ID: **1311**

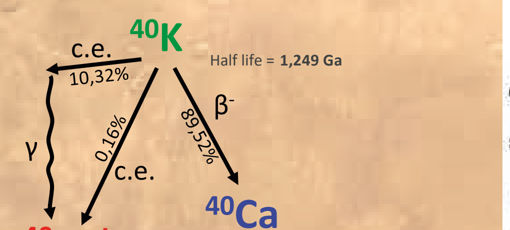
Contact: **fanny.cattani@nasa.gov**

F. **Cattani**[1,2], P.Y. **Gillot**[1], X. **Quidelleur**[1], A. **Hildenbrand**[1], B.A. **Cohen**[2]

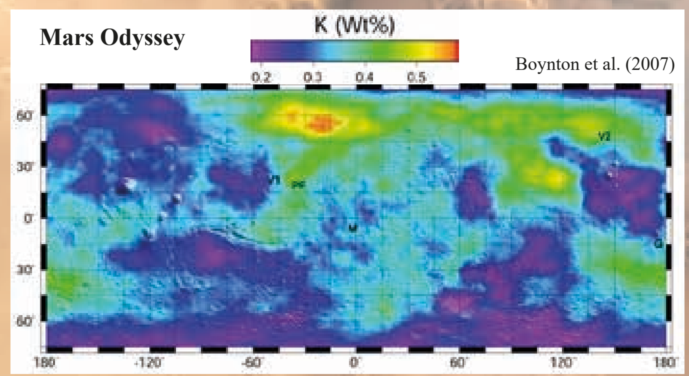
[1]Univ Paris Saclay, Univ Paris Sud, CNRS, GEOPS, Rue du Belvedere, Bat 504, F-91405 Orsay, France [2]NASA Goddard Space Flight Center, Greenbelt MD 20771

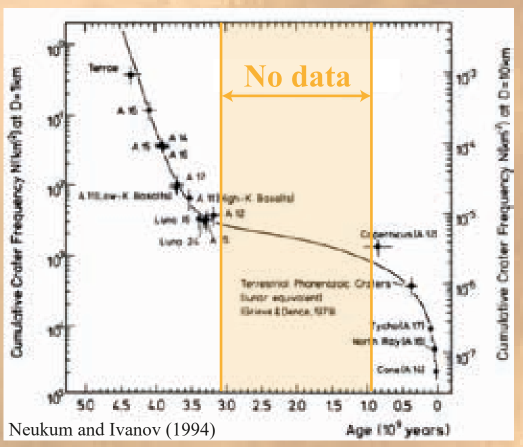

## Principle

Absolute age determination is necessary to **check and calibrate the relative Martian chronology** presently available from meteoritic crater counting.




$$t = \frac{1}{\lambda} \times \ln\left[\frac{^{40}Ar^*}{^{40}K} \times \left(\frac{\lambda_{ce} + \lambda_{\beta}}{\lambda_{ce}}\right) + 1\right]$$




K-Ar dating method is particularly suitable for such purpose.

It is based on the radioactive decay of $^{40}K$, a **major element universally distributed**. Its daughter, $^{40}Ar$, noble gas, which accumulates as a function of time.

The **measurement of K and $^{40}Ar$** can be used for ***in-situ*** **dating planetary surface** rocks as long as the ***sample mass from which they were extracted is known***.

We present here an **in-situ K-Ar dating prototype, KArMars**[1], based on **UV-laser** ablation, K measurement by **LIBS**, and argon analysis by **QMS**.

## Reference samples

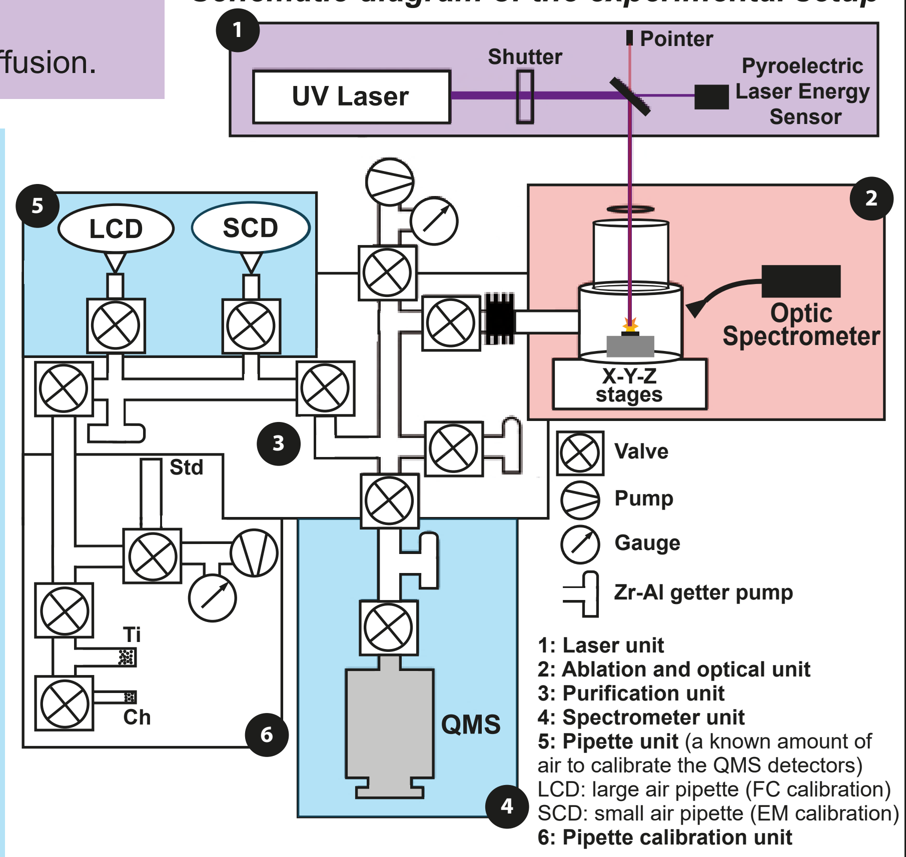

Instrument calibration, and checking measurements reliability for Martian analyses, **requires terrestrial analogues**.

For such purpose, analyses have been performed in order to qualify **mineralogy**, **K%**, and **$^{40}Ar$ content** from a collection of old terrestrial rocks[1].

## Features and Calibration

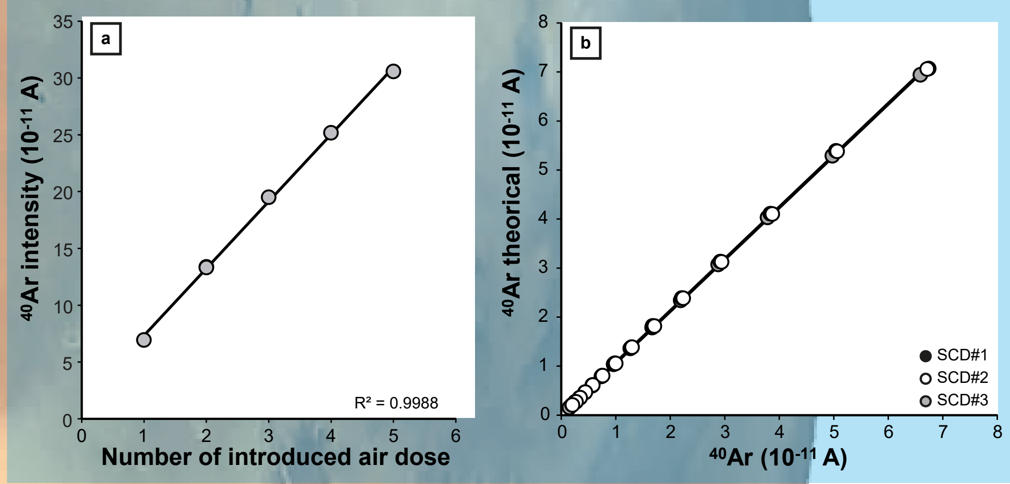
**Laser unit** with a Q-switched Spectra Physics **Nd-YAG / 14 ns / 10 Hz / 266 nm**
Evapore a specified amount of sample without significant argon diffusion.

***Schematic diagram of the experimental setup***




**SXP Elite V QMS**
EM sensitivity **$1.47\times10^{-21}$ A/atom**

Several air pipette analyses were conducted and highlighted the **linearity of the QMS instrument** in the range **0.2 to $30\times10^{-11}$ A**, corresponding to a range from $9.7\times10^{8}$ to $1.7\times10^{11}$ atoms of $^{40}Ar$.




**Ocean Optics HR2000+** / gate: **385-835 nm** / resolution: **0.23 nm**

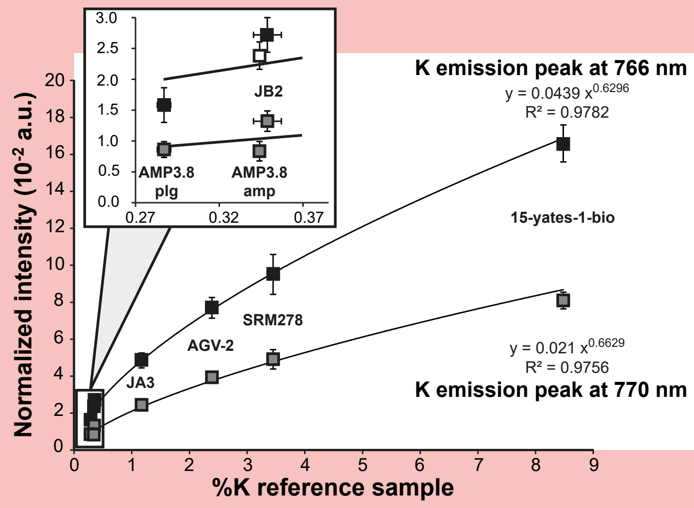
**Univariate analysis** was selected to define a **correlation between the LIBS signal** and a **known concentration** using **calibration curves** based on standards analyses (glasses and reference samples).

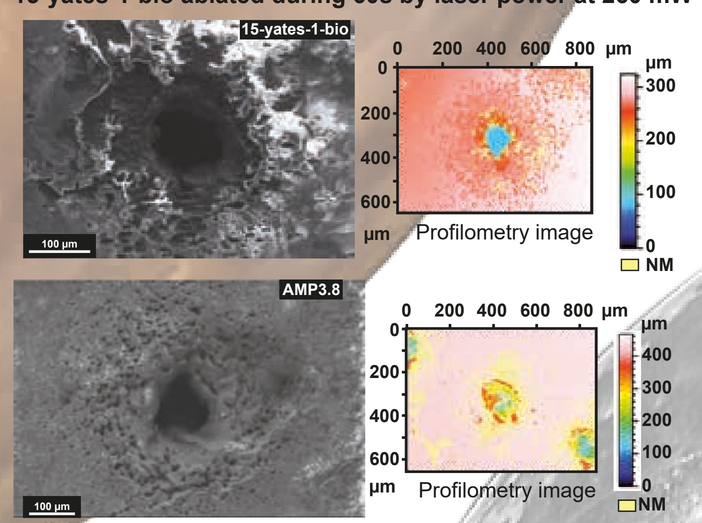
The **non-linear trend** can be explained by **self-absorption**, the decreasing plasma luminosity and/or **matrix effects**[2-4].

**Limits of detection and quantification**

LOD766: 0.14% LOD770: 0.05%

LOQ766: 0.52% LOQ770: 0.19%

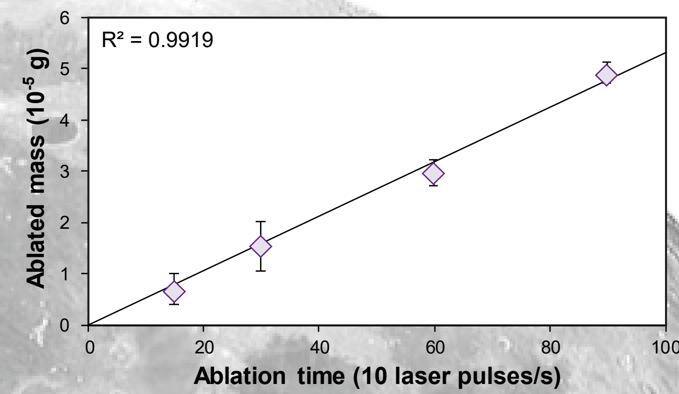


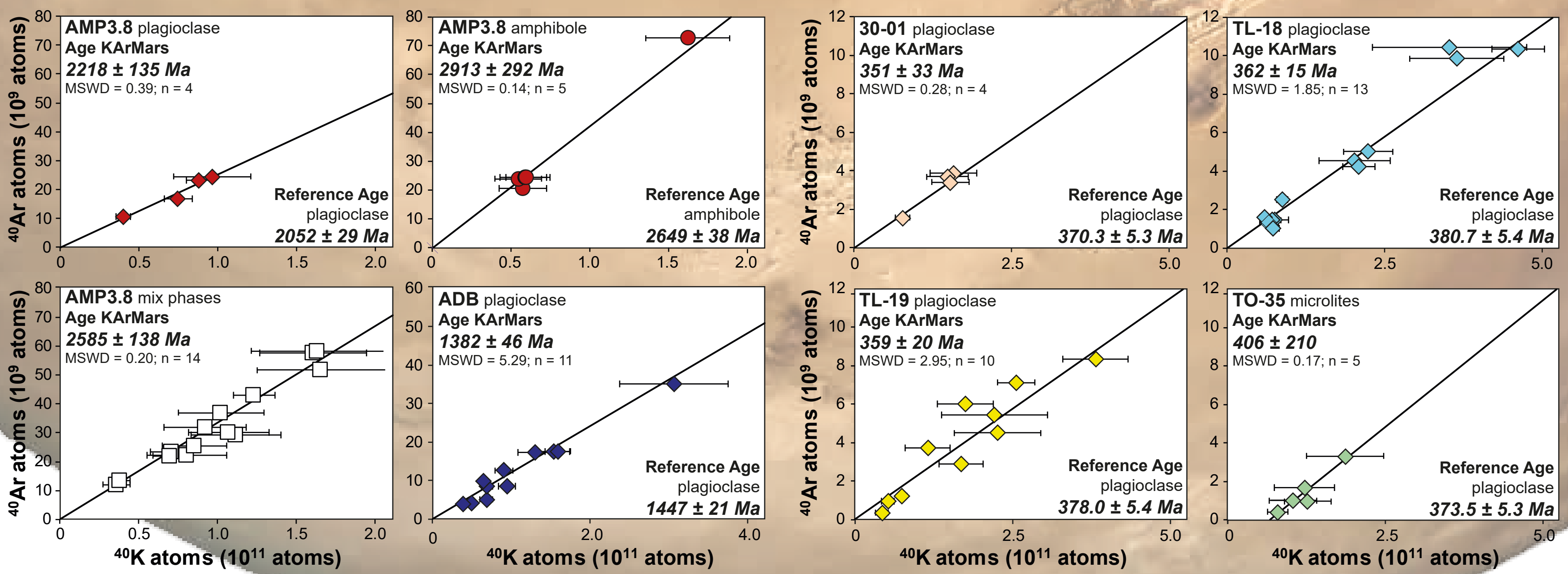

The ablated mass determination depends on **laser parameters**, and on **the mineral analyzed**. The **profilometry technique** can define this mass[5-7] but this technique can be affect by several parameters[1].
**In this study the mass determination is based on the QMS measurements.**

Several analyses of reference plagioclases allowed us to define **the relation between the ablation time and the ablated mass.**

Indeed, the relation is obtained by comparison between QMS signal and **the known content of $^{40}Ar^*$ atoms per gram** of the reference.




## Application




UV laser ablations were performed on **AMP3.8**, **ADB**, and **30-01**, **TL-18**, **TL-19**, **TO-35** (basalt from Viluy) used here as **unknowns**. The error bars on each point are defined by the uncertainties on K% (between **5 and 40%**), mass (around **4%**) and $^{40}Ar$ (less than **2%**) measurements[1].

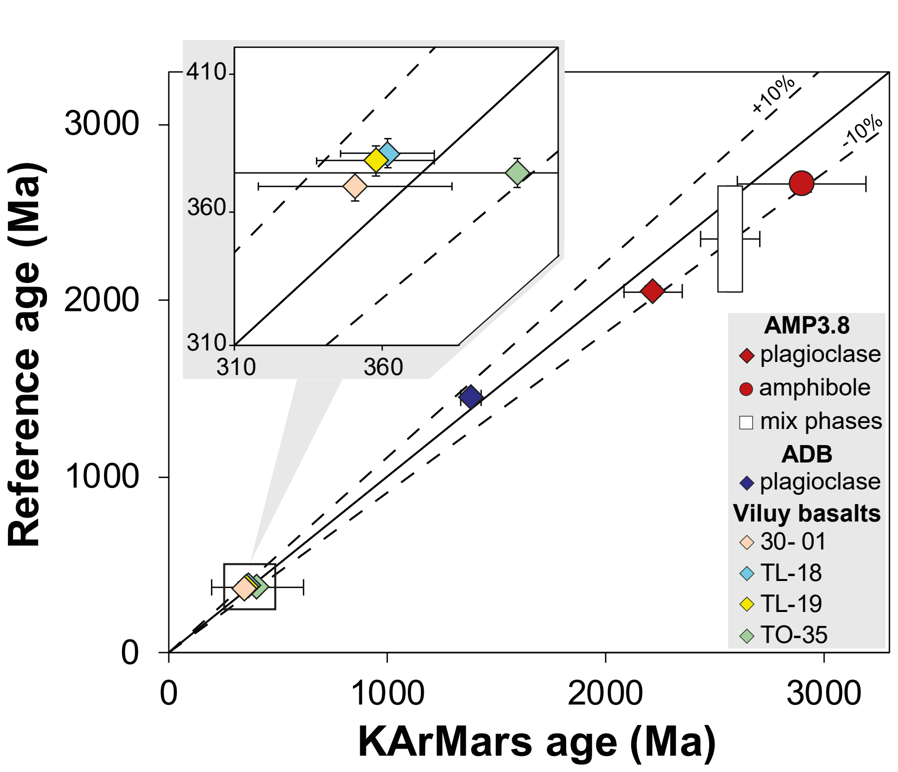
In order to reduce this uncertaincy, KArMars ages of these samples have been determined using the **isochron approach**[8] with the following equation:

$$^{40}Ar = {^{40}Ar_i} + (\lambda_e / \lambda) \times {^{40}K} \, (e^{\lambda t} - 1)$$

Where λ is the total decay constant of $^{40}K$, and $\lambda_e$ is the decay constant of $^{40}K$ to $^{40}Ar^*$

here $^{40}Ar_i$ represents the intercept on the y axis (b) and $(\lambda_e/\lambda)(e^{\lambda t}-1)$ represent the slope (m) which is a function of the age. Thus $t = 1/\lambda \times \ln[m (\lambda / \lambda_e) + 1]$.

That allows to obtain an **uncertainty and an accuracy lower than 10%**. This is even observed for relatively young and low K samples from Viluy basalts, which are at the **limit of detection** of the instruments[1].




## Perspectives

B.A. Cohen's team develops a device based on the same principle, **KArLE**[5], at NASA GSFC

### DALI project

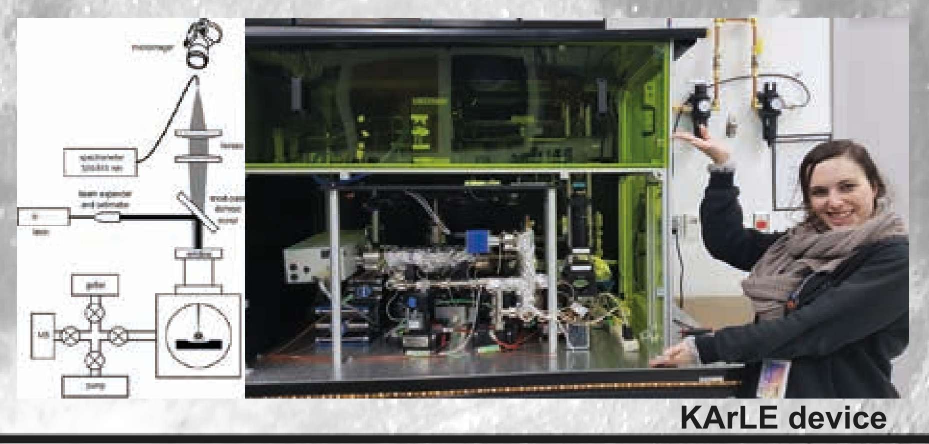
The **agency's Development and Advancement of Lunar Instrumentation**, or DALI, program recently awarded funding to mature spacecraft-based instruments for use in **future lander missions**.

Knowing the precise ages afforded through potassium-argon dating would help scientists understand the **Moon's history, its formation, the effects of bombardment, and by extension, the history of the solar system. KArLE is an especially good match to the DALI call** because all of the **necessary components have been proven on flight missions**.

As part of the DALI project, we need to **miniaturise KArLE** and **calibrate the instruments for the moon**.

### PLS method[9]

The intensity of each elemental peak is **not a simple function of elemental abundance**. Furthermore, LIBS data is sensitive to the composition of the sample. PLS method helps **understand the bulk composition** of the sample and **refine the K calibration curve** better than univariate analysis.



KArLE device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