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

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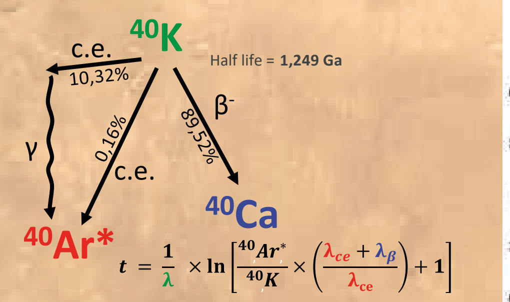
Contact: **fanny.cattani@nasa.gov**

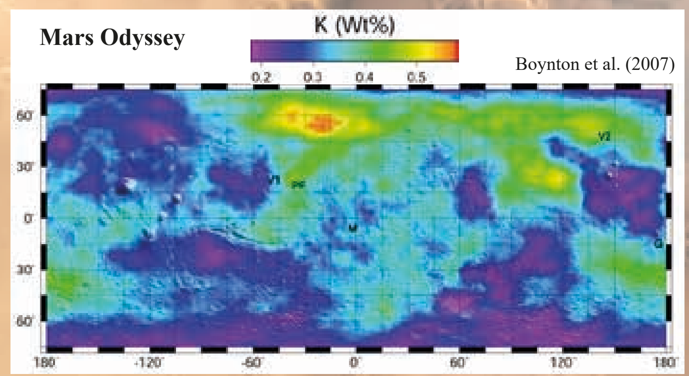
F. **Cattani**[1,2], P.Y. **Gillot**[1], X. **Quidelleur**[1], A. **Hildenbrand**[1], B.A. **Cohen**[2]

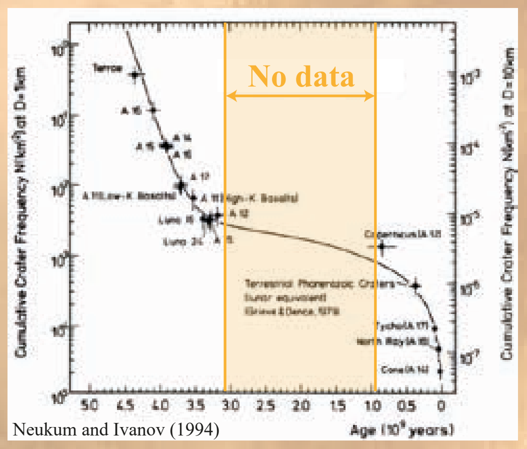
[1]Univ Paris Saclay, Univ Paris Sud, CNRS, GEOPS, Rue du Belvedere, Bat 504, F-91405 Orsay, France [2]NASA Goddard Space Flight Center, Greenbelt MD 20771

Principle

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







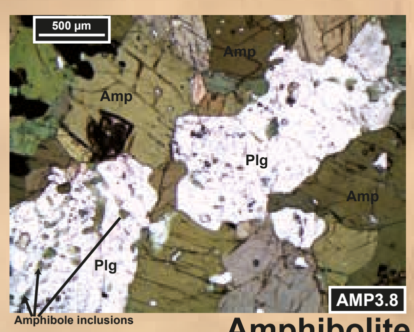
K-Ar dating method is particularly suitable for such purpose.

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.

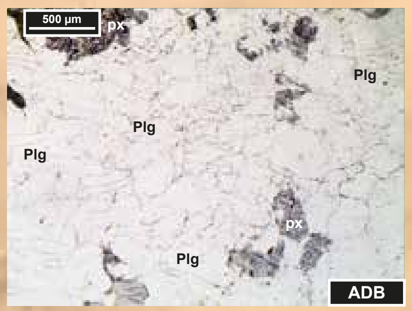
The **measurement of K and ^{40}Ar** can be used for ***in-situ* dating planetary surface** rocks as long as the ***sample mass from which they were extracted is known***.

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



Amphibolite



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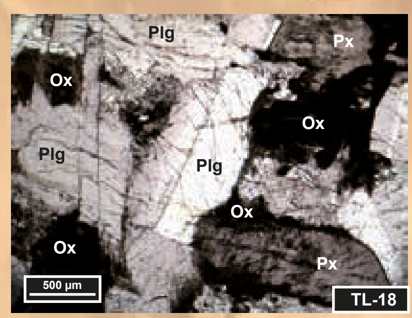
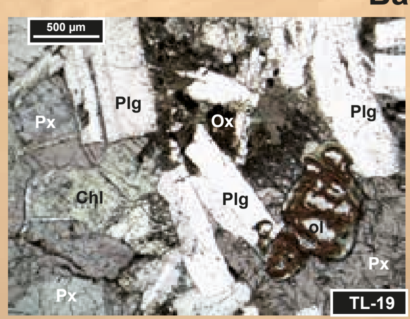
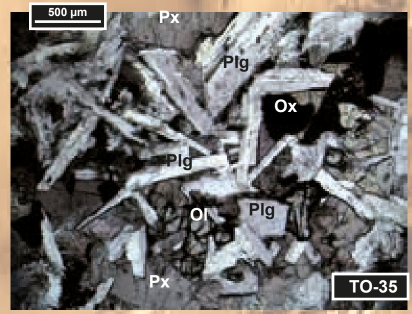


Basalts





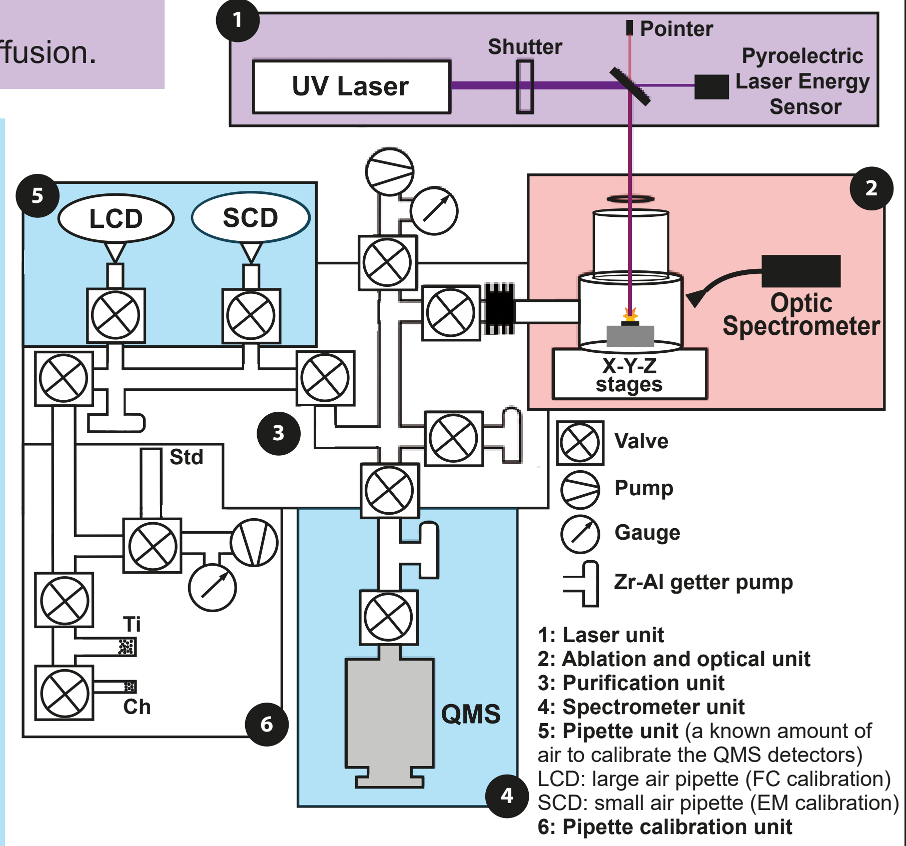
Instrument calibration, and checking measurements reliability for Martian analyses, **requires terrestrial analogues**.

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

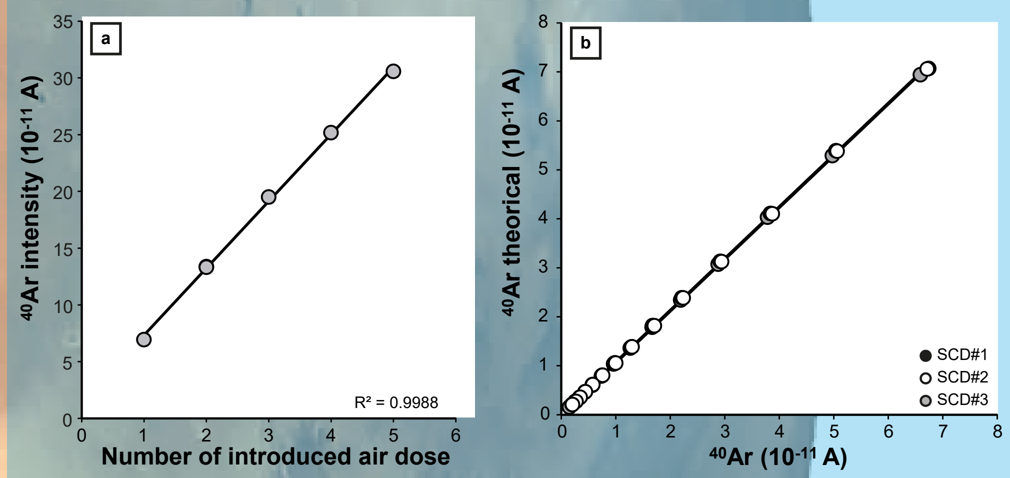
Laser unit with a Q-switched Spectra Physics **Nd-YAG / 14 ns / 10 Hz / 266 nm**
Evapore a specified amount of sample without significant argon diffusion.

Schematic diagram of the experimental setup



SXP Elite V QMS
EM sensitivity **1.47×10^{-21}A/atom**

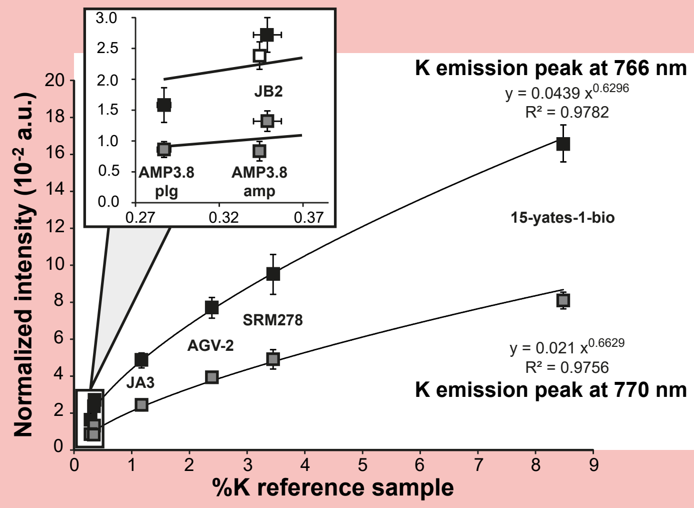
Several air pipette analyses were conducted and highlighted the **linearity of the QMS instrument** in the range **0.2 to 30×10^{-11}A**, corresponding to a range from 9.7×10^{8} to 1.7×10^{11} atoms of ^{40}Ar.



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

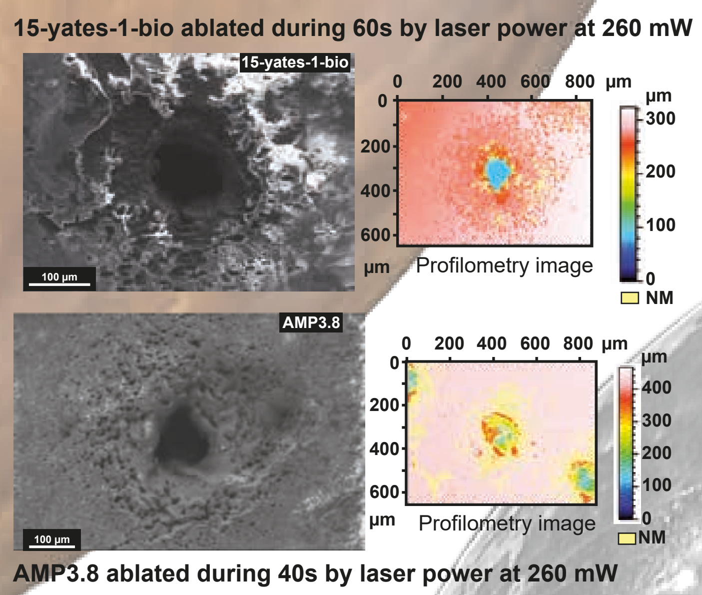
Univariate analysis was selected to define a **correlation between** the **LIBS signal** and a **known concentration** using **calibration curves** based on standards analyses (glasses and reference samples).

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

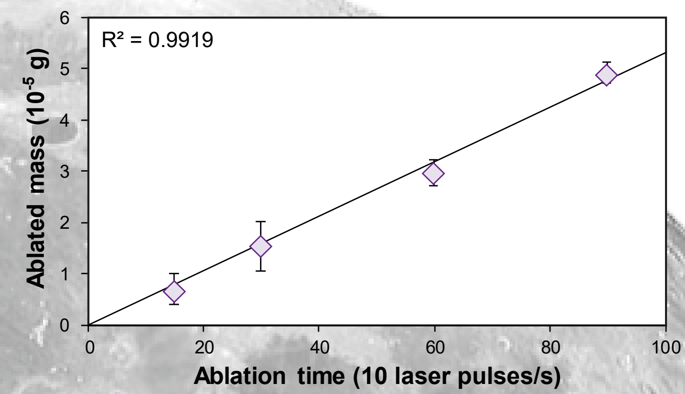
LOD_{766}: 0.14% LOD_{770}: 0.05%
LOQ_{766}: 0.52% LOQ_{770}: 0.19%



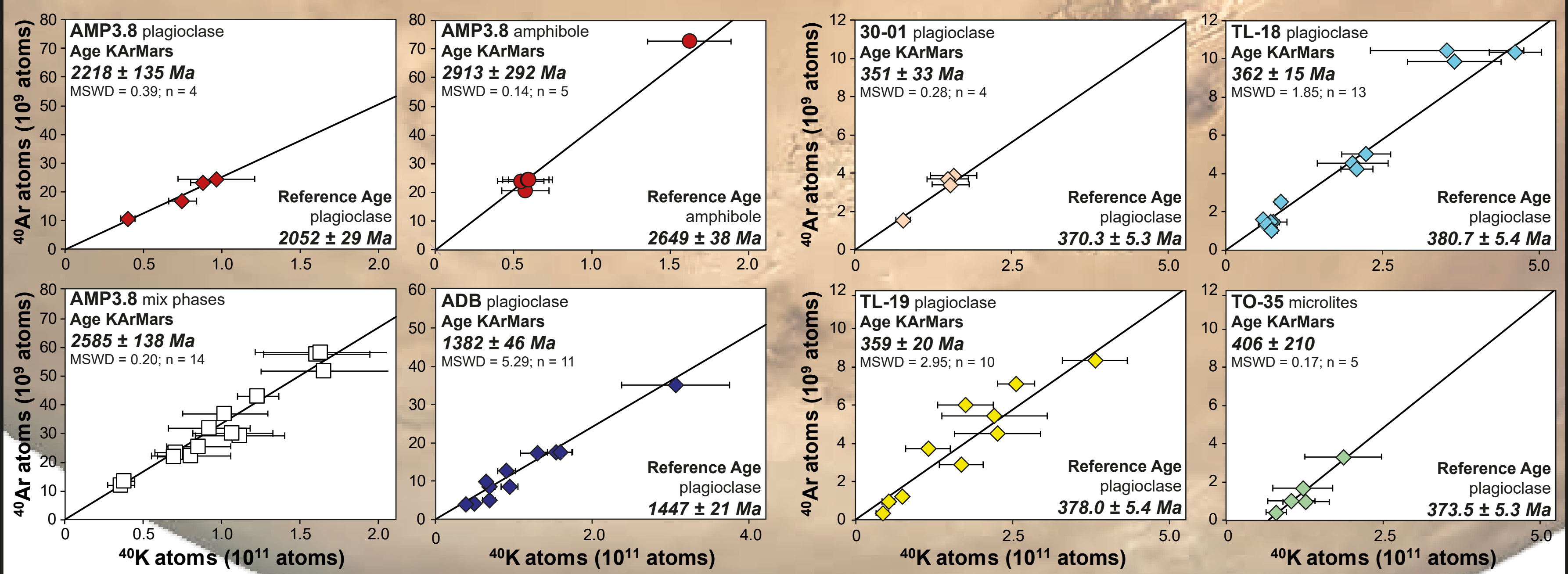
The ablated mass determination depends on **laser parameters**, and on **the mineral analyzed**. The **profilometry technique** can define this mass[5-7] but this technique can be affect by several parameters[1].
In this study the mass determination is based on the QMS measurements.

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].

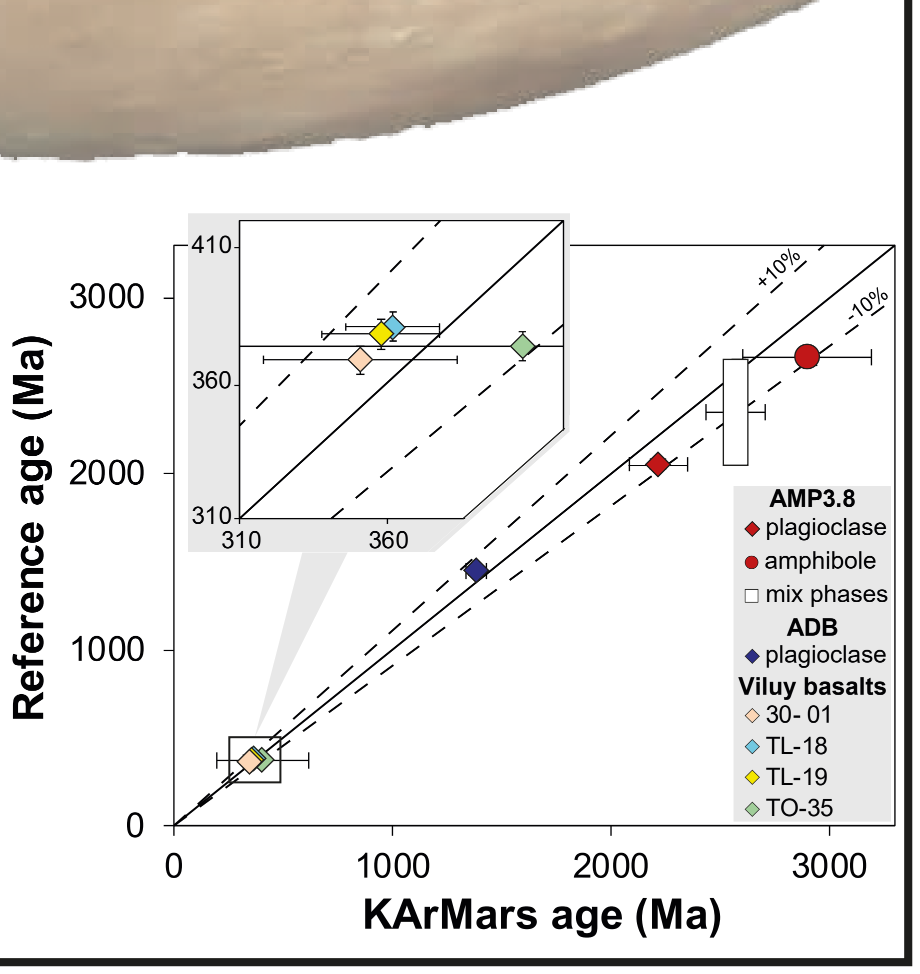
In order to reduce this uncertaincy, KArMars ages of these samples have been determined using the **isochron approach**[8] with the following equation:

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

Where λ is the total decay constant of ^{40}K, and λ_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

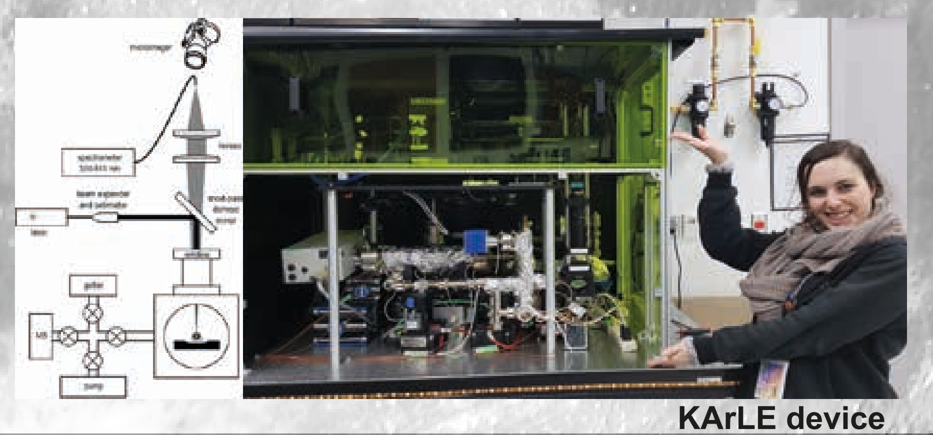
The **agency's Development and Advancement of Lunar Instrumentation**, or DALI, program recently awarded funding to mature spacecraft-based instruments for use in **future lander missions**.

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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