

## IN-SITU K-AR DATING ON MARS BASED ON UV-LASER ABLATION COUPLED WITH A LIBS-QMS SYSTEM: DEVELOPMENT, CALIBRATION AND APPLICATION OF THE KARMARS INSTRUMENT.

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**Introduction:** Absolute dating is needed to check and calibrate the relative Martian chronology presently available from meteoritic crater counting.

Recently, several experimental settings based on spot laser analyses have been developed to investigate the feasibility of in-situ K-Ar dating in future landing planetary missions [1-6]. These studies have advanced the LIBS-MS (laser-induced breakdown spectroscopy-mass spectrometry) technique but have important limitations related to the uncertainty associated with measuring the mass of the sample. In this work, we develop a new technique for estimating sample mass based on the gas release from ablation of known minerals, which may significantly improve the sample mass estimation and uncertainty. In order to reach these objectives, we present here a CNES-CNRS research program, KAr-Mars, an instrument based on UV-laser ablation to vaporize a reproducible volume of rock or mineral. It quantifies K content by LIBS and Ar by QMS.

**Reference sample:** Instrument calibration, and checking measurements reliability for Martian analyses, requires terrestrial analogues. For such purpose, total chemistry, electron microprobe analyses, flame absorption spectrometry and mass spectrometry have been performed in order to qualify mineralogy, K concentration, and Ar isotopic composition from a collection of old terrestrial rocks. These new analyses coupled with published data allowed us to select mineral phases (e.g. feldspars, phlogopite, muscovite, amphibole) showing a large range of K content (0.3-8.5wt%). All these mineral phases display a K-Ar age older than 300 Ma. Hence, the radiogenic <sup>40</sup>Ar content (in atoms per gram) falls within the range of 1 Ga old Martian basalts with a typical K content of 0.4% (Fig.1).

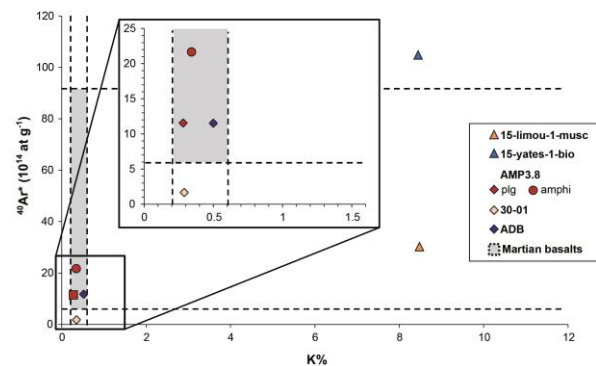


Fig.1: Number of Ar atoms per gram versus K% for standard samples. The grey bar shows expected martian values [7].

**K and Ar measurement:** In this study, univariate analysis was selected to define the correlation between LIBS signal and concentration for each element. Standard glasses and our new reference samples were selected to define calibration curves (Fig.2). The overall non-linear trend (Fig. 2) can be explained by self-absorption, the decreasing luminosity of the plasma and/or physical/chemical matrix effects [2;8-10].

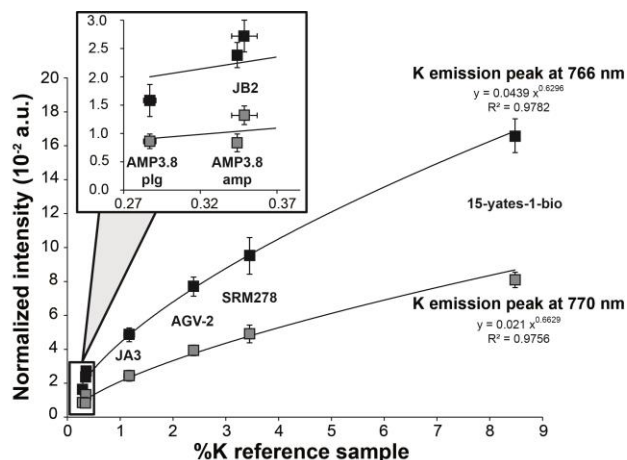


Fig.2: Calibration curves for the potassium doublet at 766nm and 770nm under vacuum conditions ( $10^{-8}$  mbar). The emission line at 766 nm is selected when there is no interference line (with Mg and Fe peaks [1;8]).

The limit of detection (LOD) and the limit of quantification (LOQ) of K determinations are derived from these calibration curves. For the 766 nm peak, they are 0.14 and 0.52 wt.%, respectively, and for the 770 nm peak, they are 0.05 and 0.19 wt.% [11].

As a very small amount of sample is evaporated during ablation (between 10 and 50 $\mu$ g), the <sup>40</sup>Ar was measured with an electron multiplier (EM). The EM sensitivity is defined at  $1.47 \times 10^{-21}$  A/atom and its quantification limits at  $3 \times 10^8$  atoms ( $5 \times 10^{-16}$  mol). The uncertainty defined by the relative standard deviation on the signal, is lower than 1% for <sup>40</sup>Ar. Several experiments were conducted and highlighted the linearity of the QMS instrument in the range 0.2 to  $30 \times 10^{-11}$  A, corresponding to a range from  $9.7 \times 10^8$  to  $1.7 \times 10^{11}$  atoms of <sup>40</sup>Ar, which is much wider than typical signals expected for the analogue samples of the Martian rocks.

**Determination of ablated mass:** Our main challenge is to determine the ablated mass, which depends

on laser parameters, and on the mineral analyzed. In contrast to the  $^{40}\text{Ar}/^{39}\text{Ar}$  technique, this mass is needed as conventional K-Ar measurements compare absolute values of K content and radiogenic  $^{40}\text{Ar}$  amount per gram of sample.

The mass determination based on a profilometry technique is used on several in-situ dating studies [3-5]. This technique can be affected by different parameters (e.g. mineral strength, density determination, surface color, shape and/or visibility of the crater bottom) directly affecting volume and mass determinations [1]. Consequently, in this study, we rely only on a volume determination based on QMS measurements of reference minerals, which can provide mass measurements from the released amount of  $^{40}\text{Ar}$  with a relative uncertainty as low as 2%. For this purpose, several analyses of plagioclase crystals of ADB, AMP3.8 and 30-01 allowed us to define the relation between the ablation time and the ablated mass (Fig. 3). The ablated mass is obtained by comparison between the number of atoms measured by QMS and the known content of  $^{40}\text{Ar}^*$  atoms per gram [1]. The uncertainty was defined from the relative dispersion of average data obtained for each sample for given ablation time, and the uncertainty on the slope of 4% is obtained following [12].

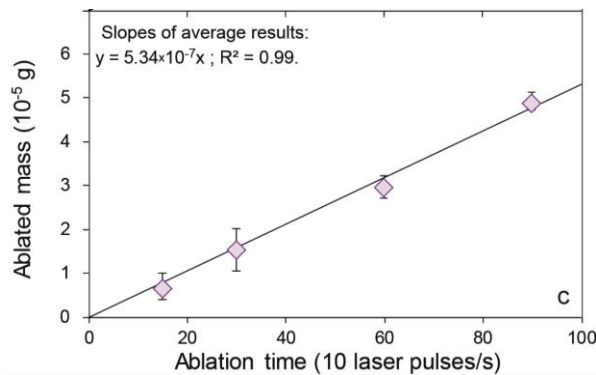


Fig.3: Correlation line between the ablated mass obtained via QMS data and the ablation time.

**Using KArMars for in-situ dating:** In order to test the KArMars instrument for in-situ K-Ar dating, terrestrial analogues to Martian rocks with a large range of crystals size have been selected [1]. UV laser ablations with 150 to 900 laser pulses were performed on AMP3.8, ADB, and 30-01, TL-18, TL-19, TO-35 (basalt from Viluy Traps) used here as unknowns. The main source of age uncertainty is due to the LIBS measurements, as K uncertainties range between 5 and 40%. The uncertainty on  $^{40}\text{Ar}$  measurement is about 2%, and the uncertainty on mass determination obtained using reference samples, is about 4% [1]. Propagating these independent sources of uncertainty yields a relative age uncertainty between 7 and 40% for a

typical single ablation. In order to reduce this uncertainty, KArMars ages of these samples have been determined using the isochron approach that allows to obtain an uncertainty lower than 10%. The comparison shown in Fig. 4 highlights the accuracy of KArMars ages, which are all within 10% only of their reference age. This is even observed for relatively young and low K samples from Viluy basalts, which are at the limit of detection of the instruments composing the KArMars setting [1].

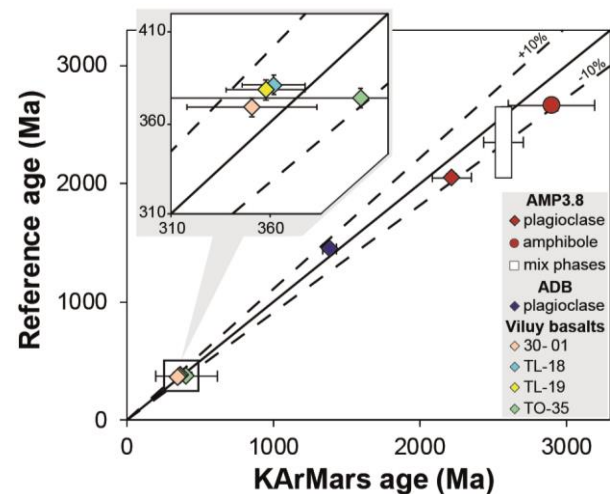


Fig.4: Comparison between reference and KArMars ages on AMP3.8, ADB and Viluy basalts.

**Conclusion:** In this study, we developed and calibrated an in-situ K-Ar dating instrument (KArMars) based on LIBS for K measurements, QMS for Ar determinations, and analyses of reference samples for calibration of the ablated mass. Our results show that the KArMars approach can be successfully used for dating a large compositional range of Martian rocks, with uncertainties as low as about 10%, and with accuracy of 10%.

**References:** [1] Cattani F. et al. (2019) *Chem. Geol.* [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. and Geoanal. Res.*, 40, 517–532. [6] Solé J. et al. (2014) *Chem. Geol.* 388, 9–22. [7] Boynton W. (2007) *J. Geophys. Res. Planets*, 112(E12). [8] Cho Y. et al. (2015) *Spectrochim. Acta B At. Spectrosc.* 106, 28–35. [9] Cremers D.A. and Radziemski L.J., “Handbook of LIBS”, 2006. [10] Guezenoc J. et al. (2017) *Spectrochim. Acta B At. Spectrosc.* 134, 6–10. [11] Mermet J.M. (2008) *Spectrochim. Acta B At. Spectrosc.* 63, 166–182. [12] Mahon J.M. (1996) *Int. Geol. Rev.* 38, 293–303.