IN SITU DATING EXPERIMENTS OF IGNEOUS ROCKS USING THE POTASSIUM–ARGON LASER EXPERIMENT (KArLE) INSTRUMENT: A CASE STUDY FOR ~380 MA BASALTIC ROCKS.

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Introduction: The in situ geochronology experiments conducted by the Curiosity rover on Mars underlined the importance of acquiring absolute age data along with other geochemical data [1–3]. At the same time, the results revealed some challenges involved with this technique, such as the difficulty in extracting ^{40}Ar from highly retentive minerals and the incapability of directly measuring the sample mass. Furthermore, the bulk analyses of powdered samples would dilute small and rare K-rich phases with the predominant K-poor minerals during the powdering process, hindering the accurate age measurements of such samples.

To resolve these problems and expand the capability of in situ geochronology, several groups including ours have been developing K–Ar dating instruments based on a laser-ablation approach [4–11]. In this technique, laser pulses vaporize the sample surface, liberating K and Ar very locally (hundreds of microns in diameter and depth). The concentrations of K and ^{40}Ar in the laser spots are measured with laser-induced breakdown spectroscopy (LIBS) and mass spectrometry (MS), respectively (LIBS–MS approach).

The K–Ar Laser Experiment, KArLE, implements this analysis using components common to most planetary surface missions [4]. In fact, LIBS, MS, and micro-imaging instruments were aboard Curiosity as ChemCam, SAM, and MAHLI, respectively. Using these flight-heritage components reduces the cost, time, and risk of hardware development.

So far, a couple of proof-of-concept studies have shown that the LIBS–MS analysis of heterogeneous rocks allows for constructing isochrons [4, 6]. These studies, however, did not measure samples typical on planetary bodies. For example, the terrestrial rocks measured in Cho et al. [6] were very K-rich, coarse-grained, and heterogeneous gneisses. Although these rocks are favorable for K–Ar dating, the majority of planetary surface is covered with basaltic rocks, which are typically much K-poorer and much more homogeneous. The capability of isochrons could be limited when such rocks are measured in actual missions. Thus, the capability of the LIBS–MS approach needs to be assessed for basaltic rocks to further validate its performance as an in situ dating technique. Here we conduct a series of case-study experiments with an instrument suite equivalent to flight devices, to show the accuracy and precision that KArLE can achieve at a realistic situation.

Experimental: *KArLE breadboard.* We used the breadboard model developed in Cohen et al. [4] with some upgrades. Major upgrades include the following: (1) the pulse energy of the Nd:YAG laser was attenuated to 30 mJ to simulate the laser equipped with Curiosity, (2) the spectrometer shutter was synchronized with the laser pulses to reduce the dark noise of the emission spectra. The exposure time was set at 1 ms.

Samples. Two ~380 Ma basaltic rocks (TL–18 and TL–35 [12]) from Viluy traps, Siberia, were measured with the KArLE breadboard. Each sample was cut into a slab and placed in the analysis chamber. The density of the rocks was measured to be 2.8 ± 0.2 g/cm^3.

Protocols. The KArLE vacuum chamber was baked at 150°C for 48 h before measurements. We analyzed 13 spots for TL–18 and 10 spots for TO–35. Five hundred laser pulses were applied on each spot. The gas liberated from the samples was purified for 5 min by the getter heated at 400–450°C. The purified gas was then admitted to a quadrupole mass spectrometer (QMS) in a static operation. The volume of the laser-ablation pits was measured externally with a laser microscope as described in [4].

Data analysis. The concentration of K in each spot was determined using a calibration curve. For this calibration curve, the sum of the intensities of K emission lines at 766.5 and 769.9 nm was normalized with the total emission intensity recorded by the spectrometer. This normalization reduces the signal variation because of the inevitable shot-by-shot fluctuation of laser pulse energy, as well as of the variable emission intensity from plasma generated in laser pits. The errors of K contents were determined based on the prediction band method [6, 8].

The amount of Ar was measured with the QMS. Its sensitivity was calibrated in advance by admitting the known amount of terrestrial air into the vacuum line. The reproducibility of the sensitivity was 3.5% during the measurements of the samples. A procedural blank was measured before each gas analysis and subtracted.

Detection limits. The detection limit of K_2O was 1000 ppm based on the 1σ prediction band approach, although the K emission line at 766 nm was still detected with a 3σ level from a calibration sample containing 1300 ppm K_2O.

The detection limit of ^{40}Ar is determined by the amount of background gas, mostly C_3H_4. The background level at 40 Da was 1.4×10^{-11} cm^{3}STP. For isobaric correction at 40 Da, the ion currents at 39 Da

(C_3H_3) were measured. Then we estimated the abundance ratio of C_3H_4/C_3H_3 from the data point where no ^{40}Ar was expected. The estimated contribution from C_3H_4 was subtracted from the signal at 40 Da.

Age measurement results: The K–Ar isochron diagrams for the two rock samples are shown in Fig. 1. The slopes of the isochrons yield 380 ± 44 Ma for TL–18 and 398 ± 50 Ma for TO–35. These ages are consistent with the K–Ar ages of the plagioclase grains measured with a conventional approach (i.e., 381 ± 5 Ma for TL–18 and 374 ± 5 Ma for TO–35 [12]). Our experimental results indicate that the LIBS–MS approach achieves the precision of 50 Ma for basaltic rocks with a 1σ significance level, complying with the requirements from the Decadal Survey. Also, the accuracy of the best-fit age was better than 25 Ma, or <7%.

The intercepts of the isochrons indicate that the amount of trapped ^{40}Ar was $(11 \pm 10) \times 10^{-7}$ cm^3STP/g for TL–18 and $(9 \pm 6) \times 10^{-7}$ cm^3STP/g for TO–35. These values are consistent with the values reported in [12]. Thus the isochron approach was able to tell radiogenic ^{40}Ar from trapped ^{40}Ar, improving the accuracy of K–Ar ages.

Figure 1 also shows the spot-to-spot variation of K contents, reflecting the samples' heterogeneity on the scale of the laser spot (~400 μm in diameter × 400 μm in depth). Nevertheless, the range of the K abundance is much smaller than that of [6]. In fact, the highest K concentrations observed in this work were 2.7 wt% for TL–18 and 7000 ppm for TO–35, whereas those of two gneiss samples were 16 or 7 wt% in [6]. Also, the K_2O of 2.7 wt% for TL-18 is twice as high as its bulk K concentration of 1.1 wt%. This is most likely because the laser spot measured a small K-rich phase, which would have been diluted in a bulk analysis.

Moreover, the highest K abundances in the TO–35 isochron was 6000–7000 ppm, consistent with the K content of plagioclase in TO–35 (6400 ppm) [12]. Our results indicate that the isochron measurement yields accurate and precise ages for a sample even when plagioclase is the dominant K-rich phase. Very K-rich phases such as biotites or K-feldspars are not necessary.

The measured ^{40}Ar concentrations were on the order of 10^{-6} to 10^{-5} cm^3STP/g depending the K content of individual spot. The highest ^{40}Ar contents here are 10–30 times lower than those measured for gneisses in [6].

The volume of the laser pits was approximately 1.8×10^7 μm^3 on average, which is equivalent to ~50 μg.

Summary: Our case study using two ~380 Ma basaltic rocks indicates that the accuracy of 25 Ma and the precision of 50 Ma are achievable with the LIBS–MS approach, sufficient to address a wide range of fundamental questions in planetary science. We also confirmed that the LIBS–MS approach yields an accurate age when plagioclase is the main K-bearing phase, which further enhances the capability of this in situ dating method.

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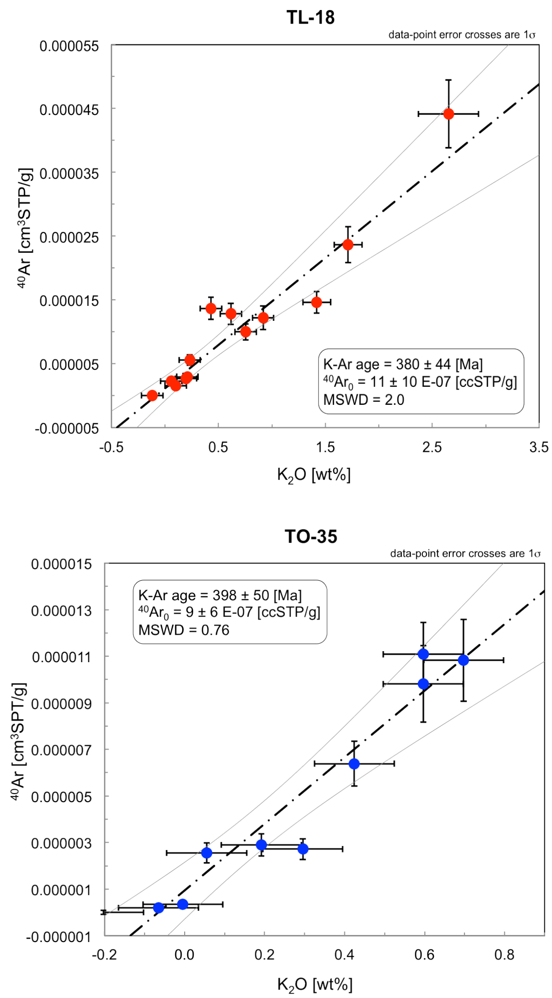

Fig. 1: K–Ar isochrons for two basaltic samples. The dashed lines indicate the best fit isochrons.

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