

# Development of an in-situ K-Ar isochron dating instrument for Mars missions: validation measurements using Martian meteorites

\*Hikaru Hyuga<sup>1</sup>, Yuichiro Cho<sup>1</sup>, Yayoi N Miura<sup>2</sup>, Takashi Mikouchi<sup>3</sup>, Haruhisa Tabata<sup>1</sup>, Koki Yumoto<sup>1</sup>, Keisuke Furuichi<sup>1</sup>, Seiji Sugita<sup>1</sup>

1. Department of Earth and Planetary Physics, The University of Tokyo, 2. Earthquake Research Institute, University of Tokyo, 3. The University Museum, University of Tokyo

**Introduction:** Martian surface ages are estimated based on crater chronology, but it has uncertainties of up to 1 Gyr due to the lack of radiometric age data for its calibration [1]. Absolute dating is essential to determine the timing of ancient warm and wet climates and the evolution of volcanic activity [2]. In situ measurements by a rover are advantageous because of their capability to measure multiple samples from various geologic units during exploration. In addition, one-way missions would be less expensive and thus presumably more frequent than sample return missions.

Potassium-Argon (K-Ar) dating is one of the promising techniques for accurate in-situ age measurements. The technique involves irradiating samples with a pulsed laser beam of several hundred  $\mu\text{m}$  in diameter in a vacuum chamber. It utilizes laser-induced breakdown spectroscopy (LIBS) for potassium (K) analysis and mass spectrometry (MS) for argon (Ar) analysis [3, 4]. Internal isochrons can be generated by measuring multiple spots to increase the reliability of age data. The successful measurements of K-Ar ages for K-rich terrestrial rocks [4] and Ar-rich chondrites [5] suggest its potential applicability on Mars. However, studies of Martian meteorites show that both contents of K and Ar would be moderately low for Martian samples (<3000 ppm [6]) due to the younger formation age (<1.5 Ga [7]). Since the measurement precision generally decreases for such samples, it is imperative to directly assess the applicability of K-Ar dating on Mars through measurements of Martian analogues.

**Objectives:** In this study, we conduct laser-ablation K-Ar dating experiments using two Martian meteorites with different formation ages, to demonstrate that Mars samples can be measured with the LIBS-MS method. We also aim to identify practical issues and insights for future Mars missions.

**Method:** Thin sections of Martian meteorites, Zagami and NWA 817, were put in a vacuum chamber pumped to a pressure of  $\sim 10^{-6}$  Pa. Then, 500 laser pulses (266 nm, 25 mJ) were irradiated at each spot. Potassium concentration was measured with the emission line of K at 769 nm. To obtain K contents, internal standard calibration lines were constructed using the intensity of the oxygen line at 777 nm or continuum emission. The amount of  $^{40}\text{Ar}$  was quantified with a quadrupole mass spectrometer. The laser ablation pits were observed under a microscope to measure the excavation volume. The measurements were conducted at different spots (15-16 spots) for each sample.

We evaluated the measurement accuracies of K and Ar to be 11% ( $1\sigma$ ; >1000 ppm  $\text{K}_2\text{O}$  range) and 15%, respectively. We optimized the LIBS optics arrangement to improve the signal-to-noise ratio of LIBS spectra, leading to a 30% improvement in the measurement accuracy than that achieved by [5].

**Results:** The K-Ar isochron ages of Zagami and NWA 817 were  $166 \pm 75$  and  $1193 \pm 243$  Ma ( $2\sigma$ ), respectively. These ages are consistent with those of  $166 \pm 6$  and 1300 Ma reported in previous studies, respectively, within a margin of error [8, 9], demonstrating that Martian rocks can be measured by the spot-by-spot laser analysis.

**Conclusion:** Our results indicate that employing this instrument for Mars exploration could significantly

refine the crater age models, particularly in the 1–3 Ga range, where uncertainties in Martian crater ages are notably substantial. To improve the dating precision, it would be necessary to increase the measurement accuracy in the volume of the laser ablation pits, which dominates the measurement error of Ar concentrations.

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