**DEVELOPMENT OF AN IN-SITU K-AR ISOCHRON DATING METHOD 2: VALIDATION MEASUREMENTS WITH NATURAL ROCKS.** Y. Cho[1], Y. N. Miura[2], and S. Sugita[1,3], [1]Dept. Earth and Planetary Sci., Univ. Tokyo. (cho@astrobio.k.u-tokyo.ac.jp), [2]Earthquake Res. Inst., Univ. Tokyo, [3]Dept. Complex. Sci. & Eng., Univ. Tokyo.

**Introduction:** Age is one of the most important factors for the interpretation of the geologic record. The surface retention ages of most planetary surfaces have been estimated with crater counting (i.e., crater chronology) based on image data. However, the Martian absolute ages may have uncertainties of about a factor of 2-4 because of the lack of directly dated samples with unambiguous locality information [1].

Most recently, Curiosity conducted the first in-situ dating experiments on Martian rock and obtained 4.21±0.35 Ga for a mudstone on the floor of Gale crater [2]. However, the noble-gas analyses of shergottites have revealed significant excess $^{40}Ar$ derived from the Martian mantle, which would cause a large error for the whole-rock analyses proposed by the previous missions including Curiosity, when an igneous rock is analyzed. Furthermore, old sedimentary rocks could contain atmospheric $^{40}Ar$ because ancient Mars, such as Noachian, may have had an atmosphere as thick as 1 bar [3]. In order to solve these problems, isochron measurements are essential.

Several research groups including ours have developed an isochron-oriented in-situ dating method based on the potassium-argon (K-Ar) system for future landing planetary missions [4-7]. In our method, K and Ar in a sample are extracted by laser ablation and measured with laser-induced breakdown spectroscopy (LIBS) and a quadrupole mass spectrometer (QMS). Spot-by-spot analyses using the laser ablation technique enable isochron measurements from a single rock sample, solving the problems for the whole rock analysis methods raised by previous studies [e.g., 8].

**Experimental:** We measured a couple of gneiss slabs to examine the capability of isochron measurements for natural rocks: a hornblende-biotite-bearing gneiss (485±35 Ma) and a pyroxene-bearing gneiss (1050±10 Ma), both of which were collected from Antarctica [9].

In order to maximize the variation in K abundance, we adjusted the positions of analytical spots based on the optical images taken by a CCD camera as well as the intensity of the K emission line induced by a couple of precursory laser shots. The abundances of K and Ar, as well as the volume of ablation cavity were measured with the system we developed previously [5].

**K-Ar isochron ($^{40}Ar/^{36}Ar$-$^{40}K/^{36}Ar$ plot):** A wide variety of K and $^{40}Ar$ abundances were obtained from the LIBS-QMS measurements, reflecting the heterogeneity in a natural rock. The concentrations of K do not necessarily exhibit those of pristine minerals. Instead, LIBS analyses yielded the averaged compositions within each ablation spot when the mineral grains are smaller than the laser spot (~500 μm). When we construct a K-Ar isochron (i.e., $^{40}Ar/^{36}Ar$ vs. $^{40}K/^{36}Ar$), the data points follow a straight line well, strongly suggesting the feasibility of isochron measurements with our LIBS-QMS approach (Fig. 1). The hornblende-biotite gneiss yielded an isochron age of 640±120 Ma, which is systematically larger than the known value by ~30% but consistent with the reported K-Ar ages within 2-sigma error. From the intercept of the isochron, we obtained the primordial Ar isotopic ratio $^{40}Ar/^{36}Ar$ of 480±130, which is comparable to that of atmospheric contamination ($^{40}Ar/^{36}Ar$=296). This also suggests that the isotopic composition of trapped Ar is measurable with this approach. This ability of measuring primordial Ar isotopic ratio in magma is important because such measurements would provide insights into the evolution of the parent magma.

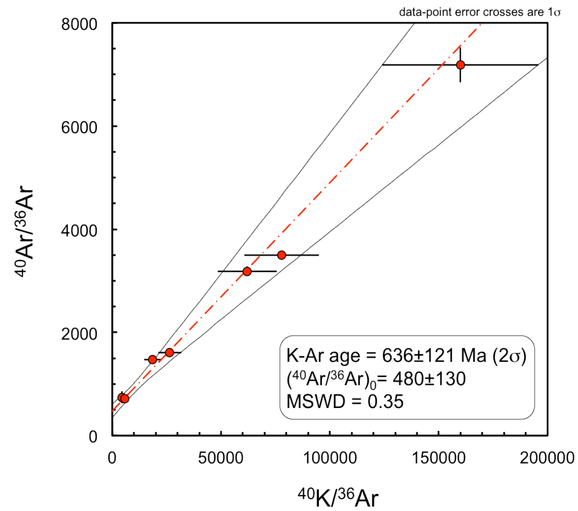


Fig. 1: K-Ar isochron for a hornblende-biotite gneiss sample. Data points follow one regression line well. The slope and the intercept yield the K-Ar age of 640±120 Ma and the initial isotopic ratio of 480±130, respectively. The error bars show 1σ error, and the errors for the isochron age and the initial isotopic ratio are 2σ uncertainties.

We also found a few important factors that could cause scatter in isochron diagram: the spallation of the laser-ablation cavity, variation in K concentrations within an ablation spot, and the contribution of blank gases to $^{36}Ar$ signal.

**$^{40}Ar$-$^{40}K$ plot and K-Ar "isochron" ages**: In contrast, the pyroxene-bearing gneiss did not contain much $^{36}$Ar derived from the terrestrial atmosphere; the amount of $^{36}$Ar was not significantly larger than the blank level. Thus, we made $^{40}$Ar-$^{40}$K plots based on the concentrations of $^{40}$K and $^{40}$Ar after checking the most of $^{40}$Ar is radiogenic in origin (Fig. 2).

The LIBS-QMS analyses yielded variable K concentrations, which is difficult to achieve with whole-rock analyses proposed in previous studies. The "isochron" slopes yielded 500±160 Ma for the 485±35 Ma sample and 1230±250 Ma for the 1050±10 Ma sample, suggesting the validity of this approach. The intercept of $^{40}$Ar-$^{40}$K plot yielded the trapped $^{40}$Ar of ~$10^{-5}$ $cm^3$ STP/g, most likely from the terrestrial atmosphere.

**Age estimation error and implications for in-situ dating on Mars:** The types of rocks and K concentration vary greatly on planetary surfaces depending on geologic units. Thus, we assess the capability of our in-situ K-Ar dating method taking the petrologic properties including K abundance and possible age range of Mars surfaces into account.

We calculated the age determination errors as a function of the concentrations of K and radiogenic $^{40}$Ar (i.e., age), based on the error propagation of K and Ar measurements (Fig. 3). The K contents and the ages of Martian meteorites suggest that dating error would be larger than 30% for shergottites due to both their young ages (<500 Ma) and low K contents (~1200 ppm), whereas the determination error would be much smaller for nakhlites because of both the older age (1.3 Ga) and the higher K contents (5000-7000 ppm). The relatively high (1-2 wt%) K content of rocks found in Gale crater or Gusev crater [10, 11] and their crater model ages [12, 13] suggest that their K-Ar ages would be measurable with 10-15% error. The K contents and the cratering ages revealed by remote-sensing satellites suggest that the lava flows in Tharsis or Elysium regions would be measured with 15-40% error depending on the age of the geologic units. If a rover finds rocks more enriched in K than those found by Gamma ray spectrometer (GRS), as Spirit and Curiosity did on their landing sites, age determination error will become much smaller.

These dating error estimations suggest that the in-situ K-Ar dating with our LIBS-QMS approach would reduce the uncertainty in Martian chronology by an order of magnitude and improve our understandings of the history of Mars greatly.

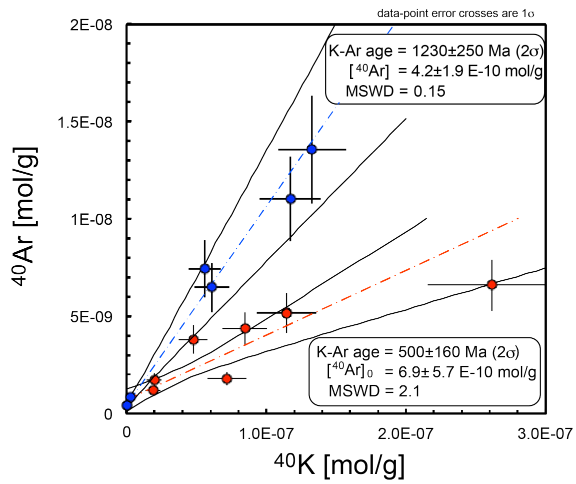


Fig. 2: $^{40}$Ar-$^{40}$K plot for (red) hornblende-biotite gneiss and (blue) pyroxene gneiss samples. The "isochron" slopes agree with the K-Ar ages determined for biotite separates with conventional methods [9]. The non-zero intercepts suggest the presence of trapped $^{40}$Ar most likely from the terrestrial atmosphere.

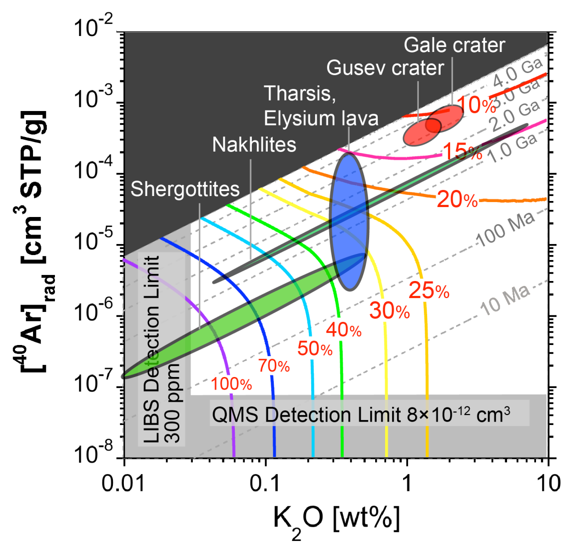


Fig. 3: Precision of our in-situ K-Ar dating method for different conditions of Martian geologic units. The concentrations of K and $^{40}$Ar for known Martian samples are illustrated by red, blue, and green ellipses, which indicate the data from rovers, orbiters, and Martian meteorites, respectively. Color contours indicate the precision of age measurements as a function of K and $^{40}$Ar abundances.

**References:** [1] Hartmann W. K. & Neukum G. (2001) *SSR*, *96*, 165-194. [2] Farley K. A. et al. (2013) *Science Express*, 1247166. [3] Phillips R. J. et al. (2001) *Science*, *291*, 2587-2591. [4] Cho Y. et al. (2011) *PERC Planet. Geo. Field Symp.*, 30. [5] Cho Y. et al. (2013) *LPS XLIV*, Abstract #1505. [6] Cohen B. A. (2012) *LPS XLIII*, Abstract #1267. [7] Devismes D. et al. (2013) *EPSC VIII*, 71. [8] Bogard D. D. (2009) *MaPS*, *44*, 3-14. [9] Iwata N. (2003) *Goldschmidt*, A182 [10] Stolper E. M. et al. (2013) *Science*, *341*, 1239463. [11] Ming D. W. et al. (2008) *JGR*, *113*, E12S39. [12] Milam K. A. et al. (2003) *JGR*, *108*, 8078. [13] Deit L. L. et al. (2013) *JGR*, *118,* 1-35.