論文の内容の要旨

Development of an in-situ K-Ar isochron dating method for landers on the Moon and Mars

(月・火星着陸機用その場 K-Ar アイソクロン年代計測法の開発)

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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. The crater chronology model has been calibrated with the radiometric ages of the Apollo samples. However, no calibration samples have been obtained for the lunar surfaces before 4 Ga (billion years ago) or between 3.0-0.1 Ga. The lack of such data led many authors to propose different models, such as Late Heavy Bombardment model [*Stöffler and Ryder*, 2001], the continuous decay model [*Neukum*, 1983], and the decreasing flux model [*Hartmann et al.*, 2007]. Furthermore, the Martian absolute ages may have uncertainties of about a factor of 2-4 because of the lack of directly dated samples with clear locality information [*Hartmann and Neukum*, 2001].

Thus, many sample-return missions have been proposed in the last several decades. However, no sample-return mission has occurred since Apollo because of its high cost and technical difficulties. Consequently, in-situ dating planetary mission without sample return is very important. In addition to the lower cost, in-situ dating is valuable because of the ability of iterative and multiple measurements while traversing the planetary surfaces. In fact, several in-situ geochronology techniques have been developed or proposed for the missions including the British Beagle 2 lander and the NASA's Curiosity rover. 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 [*Farley et al.*, 2013]. However, the noble-gas analyses of shergottites 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. In order to solve these problems, isochron measurements are essential.

This study proposes a new in-situ geochronology method that can analyze individual crystals locally using laser ablation technique, in order to construct a K-Ar isochron plot from a single rock sample. We use laser-induced breakdown spectroscopy (LIBS) and quadrupole mass spectrometer (QMS) for the measurements of K and Ar, respectively. The purpose of this thesis research is to develop and demonstrate this method by establishing individual key techniques, such as (i) accurate and precise K measurement, (ii) quantitative Ar measurements from a small laser ablation spot, and (iii) acquisitions of actual K-Ar isochron ages using a combination of flight-proven instruments.

First, we developed K measurements using LIBS. A LIBS measurement had to be carried out under a high vacuum condition necessary for mass spectrometry of a trace amount of Ar gas. One of the largest challenges for the LIBS-QMS approach is to measure K accurately and precisely because the emission of laser-induced plasma is generally very weak under high vacuum conditions [*Knight et al.*, 2000]. Although a previous study reported the results of quantitative measurements of K under atmospheric pressure [*Stipe et al.*, 2012], no study has been able to measure the concentration of K under high vacuum conditions with acceptable precisions. We constructed a sensitive detection system specific for K emission lines and used an internal normalization approach to measure K emission accurately. We obtained a precise calibration curve that can determine the K abundance down to the detection limit of K_2O=300 ppm and quantitation limit of 1000 ppm. We also evaluate the precision achievable with our approach. The precision would be 20% for a rock containing 1 wt% of K, but we suggest K-Ar age would be measurable with an acceptable precision (better than 20%) by considering the error propagation.

Second, we conducted age determination experiments with the LIBS-QMS approach based on the K calibration model we developed. We combined K measurements with Ar measurements coupled with volume measurements of laser-ablation cavities to determine the K-Ar ages for geologic samples. In order to validate this method, we measured the K-Ar model ages of the homogeneous pellet samples made of pristine minerals with known ages and K content. The validation results suggest that the LIBS-QMS approach can measure the K-Ar ages with an accuracy of better than 25% and a precision of 20% except for highly brittle materials, such as the plagioclase pellet used in this study. Spallation from laser ablation cavity on these samples prohibits an accurate age measurement because the true cavity volume cannot be measured accurately. This observation suggests the mechanical strength of the sample is important for K-Ar dating using this method.

Next, we measured a couple of gneiss slabs to verify the capability of isochron measurements for natural rocks. 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. One sample 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). These results strongly suggest that the isotopic composition of trapped Ar is measurable with this approach. This ability would provide insights into the evolution of the parent magma.

The other sample 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 drew the ^{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. 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^{-6} cm^3 STP/g, which is consistent with the amount of excess ^{40}Ar contained in the shergottites [*Bogard et al.*, 2009]. The LIBS-QMS analyses yield variable K concentrations, which is difficult to achieve with whole-rock analyses proposed in previous studies. We also found the LIBS-QMS measurements yield averaged compositions for the minerals in an ablation spot. This property suggests that a wide range of K concentrations and thus a reliable isochron can be obtained even though the variety of K-bearing phases is limited. We also identified the factors that potentially cause scattering in isochron diagram and proposed several criteria to obtain reliable isochrons: the spallation of the laser-ablation cavity, the variation of K concentrations within an ablation spot, and the contribution of blank gases to ^{36}Ar signal.

The above experimental results using test samples do not guarantee the applicability of our LIBS-QMS isochron method for actual rock samples on planetary surfaces. Depending on geologic units, the types of rocks and K concentration vary greatly on planetary surfaces. 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 the Moon and Mars surfaces into account. First, we examined the global maps of K obtained with the Gamma Ray Spectrometers onboard remote sensing satellites and found the concentrations of K and Ar of KREEPy materials are well above the detection limits of our LIBS-QMS method. Then, the elemental compositions and textures of KREEP basalt were investigated. We found that Si-rich glasses contained in mesostasis are measurable with K-Ar dating on the Moon because of the high K concentration (~7 wt%) while other minerals (i.e., pyroxene, olivine, and plagioclase) contain virtually no K. Since the textures of these samples were heterogeneous at the scale of laser spot (~500 μm), the "isochron" ages would be obtained by measuring the different portions containing K-bearing phases in various ratios. The major problem concerning in-situ K-Ar dating is partial ^{40}Ar loss due to thermal events after crystallization. This suggests that K-Ar dating only yields the lower limit for the real crystallization age. Furthermore, brecciation by impacts and contamination by solar wind will inhibit accurate in-situ dating. In order to avoid such problems and obtain meaningful age data by in-situ dating, we need to find fresh samples on planetary surfaces. Although very large drills or ablator tools would be able to solve this problem by artificially exposing fresh surfaces of rocks, finding outcrops where many rock samples have naturally exposed fresh surfaces would be better in terms of reducing cost and technical difficulty of mission plan. Thus, we searched for such outcrops on the Moon and Mars. In particular, we conduct a detailed case study with Aristillus crater, which is located at the Procellarum KREEP Terrane on the Moon in this study. On the basis of high-resolution images on the impact melt sheet of Aristillus crater, we propose that measuring fresh boulders excavated by a recent small impact (crater diameter ~100 m) is effective for correlating the age of a rock sample to a geologic unit and for avoiding the problems such as the contamination by the solar wind, the reset of the K-Ar age and later brecciations by impacts.

Finally, we evaluated how our method can constrain the absolute chronology models of the Moon and

Mars based on the precisions of age measurements achieved by this study. Assuming the K concentration found by the landing missions on Mars and cratering model ages, our method is estimated to be able to determine the age of Hesperian-Amazonian boundary with 10-15% precision and constrain the duration of volcanic activities, the timing of outflow channels formation, and the absolute age when cold and dry climate started prevailing the planet. Furthermore, the absolute age of impact melt rocks in Aristillus crater, whose ages correspond to the "missing ages" of the current lunar crater chronology model (i.e., between 3.0 Ga and 0.1 Ga), would be measured with ~20% precision when the K concentration of the glass in KREEP basalt is assumed. Then, our method would be able to discriminate the constant flux model [*Neukum*, 1983] and the decreasing flux model [*Hartmann et al.*, 2007]. The implications of in-situ dating in Aristillus crater include refining the crater chronology model, determining the age of the youngest mare basalts, which provides insights into the origin of the Moon, and understanding the dynamical evolution of the asteroids in the last 3 billion years.

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